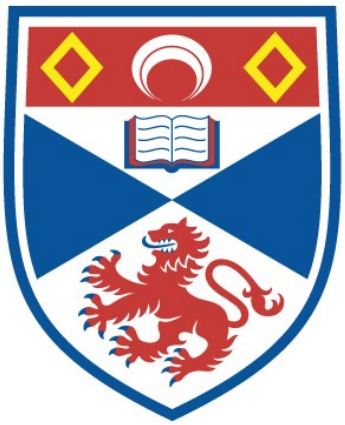
NEW VARIATIONS OF THE 1, 6, 6AΛ⁴ - TRIHETERAPENTALENE STRUCTURE

James Alexander Mitchell

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1979

NEW VARIATIONS OF THE 1, 6, 6aλ^4-TRIHETERAPENTALENE STRUCTURE

being a Thesis presented by

James Alexander Mitchell, B.Sc.

to the

University of St. Andrews

in application for

the Degree of Doctor of Philosophy

December 1979

3rd copy

DECLARATION

I declare that this thesis is based on the results of experiments carried out by me, that it is of my own composition, and that it has not been submitted previously in application for a higher degree.

December 1979 James A. Mitchell

CERTIFICATE

I hereby certify that James Alexander Mitchell, B.Sc., has spent ten terms at research work under my supervision, has fulfilled the conditions of the Resolution of the University Court, 1967 No. 1, and is qualified to submit the accompanying thesis in application for the Degree of Doctor of Philosophy.

Director of Research

UNIVERSITY CAREER

I entered the University of St. Andrews in October 1972, and subsequently graduated with Upper Second Class Honours in Chemistry in July 1976.

In October 1976 I was awarded a Science Research Council CASE Studentship, and from then until July 1979 I carried out the work which is embodied in this thesis. This work was undertaken principally in the Department of Chemistry, University of St. Andrews, under the supervision of Professor D.H. Reid. Also, in accordance with the conditions of the Science Research Council CASE scheme, I spent three months (June-August 1978) working at the Esso Chemicals Research Centre, Abingdon, under the supervision of Dr. T. Colclough.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Professor D.H. Reid for his advice, guidance and continued interest in my work. I also feel I should mention Dr. T. Colclough, my "industrial companion" at Esso Chemicals Ltd.

I would like to thank Professor Lord Tedder and Professor Wyatt for making available the excellent laboratory facilities in the Department of Chemistry, University of St. Andrews, and Esso Chemicals Ltd. for allowing me to use the laboratory facilities at the Esso Chemical Research Centre, Abingdon.

I am grateful to the technical staff of the Department of Chemistry, University of St. Andrews and to the technical staff of the Esso Chemical Research Centre, Abingdon for their invaluable assistance. Also, I am deeply indebted to Mrs. W. Pogorzelec, who prepared the typescript for this thesis.

Finally, I would like to thank the Science Research Council for the award of a CASE studentship, and to Esso Chemicals Ltd for making this CASE award possible, and for their assistance during my visits to Abingdon.

EXPLANATORY NOTE

This thesis is divided into three sections, Parts 1, 2 and 3. Each part is divided into a number of principal sections, each prefixed by a capital letter.

Part 1 consists of a review of the relevant background literature.

Part 2 consists of a discussion of the results obtained.

Part 3 consists of the experimental details of the results discussed in Part 2, and is complementary to Part 2.

Where reference is made to the chemical literature, this is indicated by a number in the superscript, a key to which can be found at the end of this thesis. The structural formulae which have been reproduced for illustrative purposes have been assigned Arabic numerals, which correspond to the numbers which have been assigned to the relevant compounds in the text. The structure keys to Parts 1 and 2 are distinct. The structure key to Part 3 is the same as that for Part 2.

CONTENTS

SUMMARY

The reaction between 3-substituted-5-phenyl-1,2-dithiolium salts and various aminoheterocycles was investigated. Substituted 2-aminopyridines gave, in most cases, a mixture of two isomeric products, formulated as dithiadiazacyclopent[a]indenes. Similarly, 2-amino-2-thiazoline and 2-aminothiazole gave a mixture of products. The effect of using different solvents and leaving groups in these reactions was studied. 4-Aminopyridine, 2-aminopyrimidine and 2-aminobenzimidazole each gave only one product, whereas 2,6-diaminopyridine produced a mixture of two disubstitution products. N-Phenylbenzamidine gave a small quantity of 5-phenyl-3-phenylimino-3H-1,2-dithiole, while 2-methylpyridine produced no useful material. Two byproducts, 5-phenyl-1,2-dithiole-3-thione and 5-phenyl-1,2-dithiole-3-one were formed in each reaction which was investigated.

2-Amino-4-methylpyridine reacted with perchloromethyl mercaptan to give a sulphenamide. Reaction of this compound with benzoylacetic acid, followed by thionation, provided an alternative route to one of the dithiadiazacyclopent[a]indene isomers. The sulphenamides of 2-amino-2-thiazoline and 2-aminothiazole failed to react with benzoylacetic acid.

1,2,4-Thiadiazoles were used to synthesise compounds formulated as 1H- and 6H-triheterapentalenes. 4,5-Dihydro-5-imino-1,2,4-thiadiazoles reacted with arenediazonium fluoroborates to give 6H-3aλ^4-thia-1,2,3,4,6-pentaazapentalenes.

4,5-Dihydro-5-imino-1,2,4-thiadiazoles formed Vilsmeier salts which reacted with aqueous methylamine or sodium hydrogen sulphide solution, producing

1H-3aλ^4-thia-1,3,4,6-tetraazapentalenes and 6H-3,3aλ^4-dithia-1,4,6-triazapentalenes respectively. Sodium hydroxide and sodium hydrogen selenide solutions failed to react with these Vilsmeier salts.

6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalenes were prepared from 5-acetamino-3-methyl-1,2,4-thiadiazole, 5-formamino-3-methyl-1,2,4-thiadiazole, 3,6-dimethyl-5-methylthio-6H-3aλ^4-thia-1,3,4,6-tetraazapentalene and from 4,5-dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole.

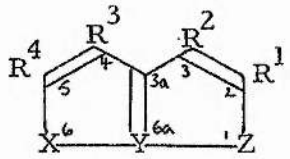
6H-3,3aλ^4-Dithia-1,4,6-triazapentalenes were prepared by thionating oxathiaazapentalenes, and by allowing carbon disulphide to react with 1,2,4-thiadiazolium salts.

An attempted synthesis of 5,6-dimethyl-6H-3,3aλ^4-dithia-1,2,4,6-tetraazapentalene from 5-amino-3,4-dimethyl-4H-1,2,4-thiadiazolium iodide proved unsuccessful.

4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole reacted with phenylisocyanate giving 2-aminophenyl-5,6-dimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalene. Phenylisothiocyanate gave 2-aminophenyl-5,6-dimethyl-6H-3,3aλ^4-dithia-1,4,6-triazapentalene. Thiophosgene gave 1,3-bis(3,4-dimethyl-1,2,4-thiadiazol-5-ylidene)acetone.

FOREWORD

1,6,6aλ^4-Triheterapentalenes may be represented by formula (I), in which X and Z are heteroatoms of Groups V and VI, and Y is a second- or lower-row element of Group VI.



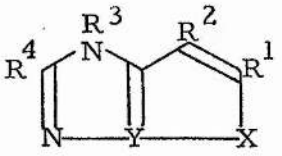
(I)

Structurally similar aza analogues arise through replacement of X, Z, or ring CH or CR units by nitrogen. Many such aza analogues, containing up to four nitrogen atoms, have been made.

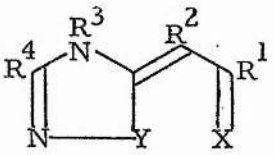
The structure of numerous trithiapentalenes has been investigated by X-ray crystallography, which has shown that the compounds are planar, with the three sulphur atoms collinear, and that some bonding is present between the sulphur atoms. Several theories of bonding have been put forward to explain the unique structural features of trithiapentalenes. The most widely accepted view invokes the formation of a four-electron three-centre bond, holding all three sulphur atoms together. According to this theory, the central sulphur atom contributes two electrons to the bond, while the two lateral atoms donate one electron each. The trithiapentalene molecule also possesses a 10π-electron system.

Reviews of the chemistry of triheterapentalenes have been written by Lozac'h[1], Klingsberg[2], Reid[3] and Beer[4-6]. The unusual structure and bonding in these compounds will be discussed more fully in Part I of this thesis.

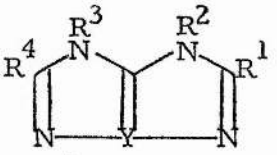
The aim of this research project was to synthesise new nitrogen-containing triheterapentalenes, especially compounds based on structures (II) and (IV). These compounds deviate from the known triheterapentalenes with respect to certain structural features, and in their bonding.



(II)



(III)



(IV)

X = O, S, NR ; Y = S

Existing triheterapentalenes possess a 10π-electron system, to which heteroatoms one and six each contribute a pair of electrons (cf. pyrrole, thiophene), (figure I). Consideration of figure II shows that the nitrogen atom in the three-centre bond

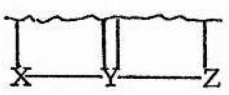


figure I

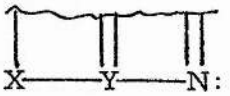


figure II

of a type (II) structure has only one electron available for π-bonding. Figure (III), which represents a type (IV) compound shows that both of the lateral heteroatoms are capable of donating one electron each to the π-system. Thus compounds of types (II) and (IV) would be

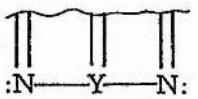


figure III

novel, in that their three-centre bonded sequences would contain pyridine-type nitrogen.

Less obviously, compounds (II) may be reformulated as the monocyclic species (III). Conclusive evidence as to whether these compounds exhibit three-centre bonding (II), or are merely substituted 1,2,4-thiadiazoles (III) is likely to be ascertained only by X-ray crystallography.

Eventually, studies of the aforementioned systems may increase the scope of our knowledge of the extent to which three-centre bonding operates in heterocyclic systems.

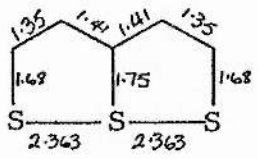
INTRODUCTION

A. STRUCTURAL STUDIES OF 1, 6, 6aλ^4-TRIHETERAPENTALENES

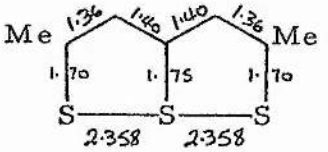
1, 6, 6aλ^4-Triheterapentalenes have been extensively investigated using the techniques for structural analysis. In particular, X-ray crystallography and nmr spectroscopy have played important roles in the elucidation of their structure.

1. X-Ray Crystallography

Crystal structure data for 1, 6, 6aλ^4-trithiapentalene (1)[7] show that the molecule is planar, with C_{2v} symmetry, and that the three sulphur atoms are collinear. The S-S bonds (2.363 Å) are approximately 10% longer than the average distance for a covalent, two-electron S-S bond[8], (2.10 Å), but they are considerably shorter than the sum of the Van der Waal's radii of two sulphur atoms[9] (3.70 Å). This indicates that significant and equal bonding interactions are present between S(6a) and S(6), and S(6a) and S(1).



(1)



(2)

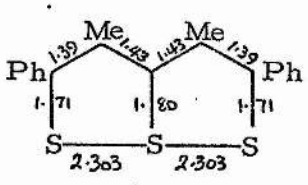
The C(2)-S(1) (1.68 Å), C(5)-S(6) (1.68 Å) and C(3a)-S(6a) (1.75 Å) distances lie between the lengths of a carbon-sulphur single bond[9] (1.81 Å) and a carbon-sulphur double bond[9] (1.61 Å), implying

that these bonds have a bond order of greater than unity. The bond lengths in the remainder of the carbon skeleton closely resemble those found in naphthalene[10], which possesses an analogous 10π-electron system.

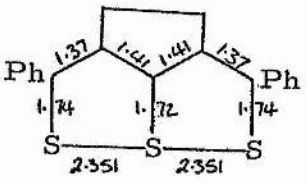
2,5-Dimethyl-1,6,6aλ^4-trithiapentalene (2) has molecular dimensions approximately equal to those of the parent compound, and exhibits similar symmetry[11-13]. Other symmetrically substituted trithiapentalenes eg. (3)[14], (4)[15], (5)[16] show C_{2v} symmetry, but compounds (6)[17], (7)[18] and (8)[19] have unequal S-S bond distances, due to intermolecular effects within the crystal lattice.

In trithiapentalene (6)[17], the phenyl groups are twisted at angles of 3° and 45° to the plane of the molecule, presumably owing to weak intermolecular interactions. An isolated molecule of (6) might be symmetrical. Compound (7)[18] is unsymmetrical due to a steric clash between the bulky phenyl groups which are in close proximity. Both types of forces probably give rise to the inequality of the S-S distances in compound (8)[19].

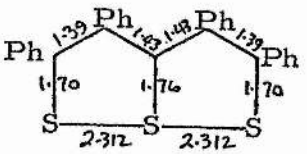
In general, trithiapentalenes with irregular substitution patterns have unequal bond lengths eg. compounds (9)[20], (10)[21,22], (11)[23], (12)[24], (13)[25], (14)[26], and (15)[27]. This indicates that the S-S distances are susceptible to intramolecular perturbation, caused, for example, by substitution. Although the individual S-S bond lengths may vary by up to 0.4 Å, the sum of the S(1)-S(6a) and S(6a)-S(6) bond distances remains fairly constant at ca. 4.7 Å, steric clashes notwithstanding.



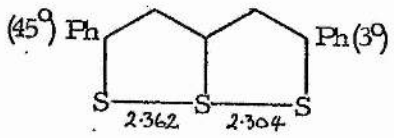
(3)



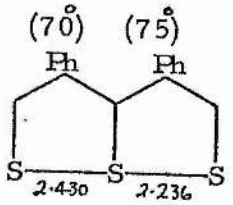
(4)



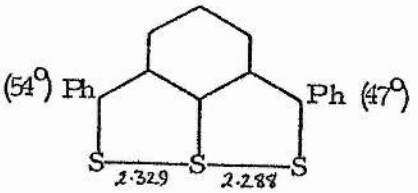
(5)



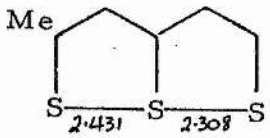
(6)



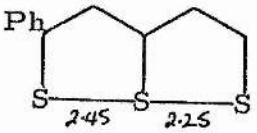
(7)



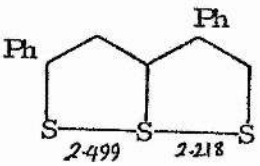
(8)



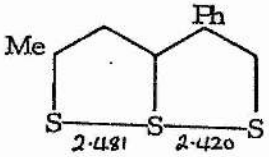
(9)



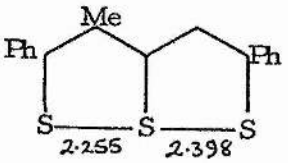
(10)



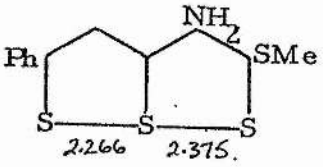
(11)



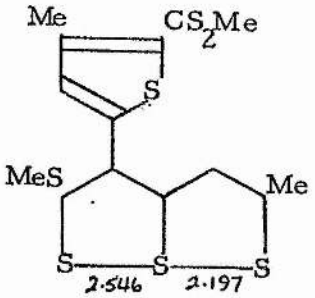
(12)



(13)



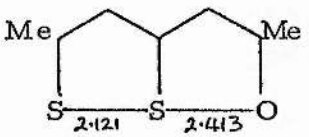
(14)



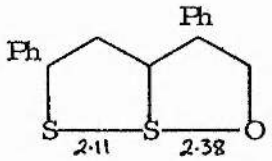
(15)

Crystal structure determinations of oxygen, selenium and nitrogen analogues of 1, 6, 6aλ^4-trithiapentalenes confirm the planar, bicyclic nature of these species.

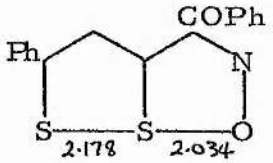
The S-S and S-O bond lengths in oxygen compounds (16)[28] and (17)[29] show that replacement of sulphur by oxygen leads to a stronger S-S interaction, and a weaker S-O interaction. These compounds may also be regarded as bicyclic. Compound



(16)



(17)



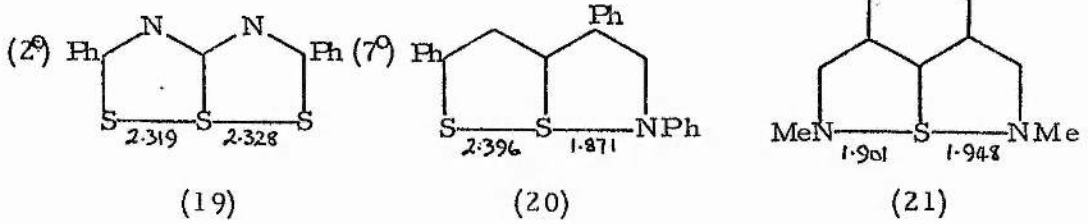
(18)

(18)[30] has a shorter S-O (2.034 Å) and a longer S-S (2.178 Å) bond length than the oxadithiapentalenes (16) and (17), and is therefore considered to be bicyclic.

The aza compound (19)[31] is unsymmetrical, probably owing to intermolecular effects involving the phenyl groups. The S-S bond distances (2.319 Å, 2.328 Å) are similar to those of the corresponding trithiapentalene (6)[17] (2.304 Å, 2.362 Å). Thus it may be assumed that compound (19) is bicyclic.

Replacing one or both of the lateral sulphur atoms in a trithiapentalene by nitrogen has a more marked effect on the corresponding bond lengths, eg. compounds (20), (21). In the 6, 6aλ^4-dithia-1-azapentalene (20)[32], the S-S-N sequence is almost linear, with an S-N bond distance of 1.871 Å (cf. the

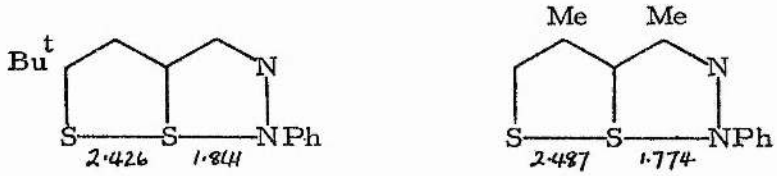
two-electron S-N covalent bond distance, 1.74 Å[9]; sum of



(19) (20) (21)

Van der Waal's radii for sulphur and nitrogen, 3.35 Å[9]). Bonding therefore exists between sulphur and nitrogen. The S-S bond length (2.396 Å) is shorter than the S-S distance in the corresponding trithiapentalene (11)[23] (2.499 Å). Compound (21)[33] shows slight departure from C_{2v} symmetry, probably because of strain induced by the trimethylene bridge, and intermolecular crystal forces. The average S-N bond length (1.925 Å) approximates to a 10% lengthening of a normal S-N bond (1.74 Å)[9], suggesting that the S-N bond order is similar to the S-S bond order found in trithiapentalenes.

Studies of the 1,2-diaza derivatives (22)[34] and (23)[35] indicate that these molecules are bicyclic. The variation in S-S and S-N bond lengths shows that substituents do affect the



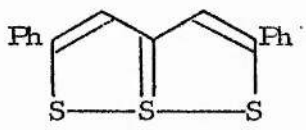
(22) (23)

bonding in the S-S-N sequence.

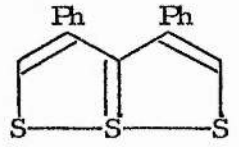
Hordvik has summarised the data from numerous other crystal structure determinations of triheterapentalenes, which have been published in the literature[21].

2. NMR Spectroscopy

The ^1H nmr spectra of all symmetrically substituted 1, 6, 6aλ^4-trithiapentalenes[36, 37] show that there is magnetic equivalence of the ring protons or substituents at C(2) and C(5), and at C(3) and C(4), indicating that these compounds possess real or time-averaged C_{2v} symmetry, in solution. 2,5-Diphenyl 1, 6, 6aλ^4-trithiapentalene (6)[36] and 3,4-diphenyl-1, 6, 6aλ^4-trithiapentalene (7)[38] exhibit this symmetry even though they

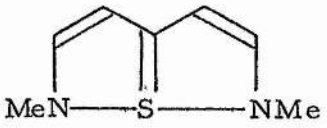


(6)

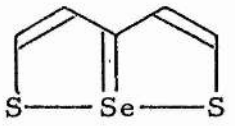


(7)

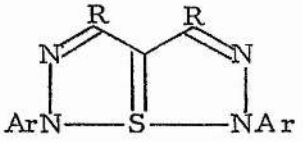
have unequal S-S bond lengths in the solid state. Trithiapentalene analogues (24)-(27)[39-42] also show real or time-averaged C_{2v} symmetry in solution. The symmetry observed in these cases may be the result of intermolecular forces being averaged out in solution.



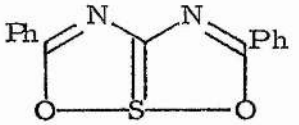
(24)



(25)



(26)



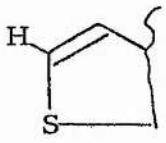
(27)

However, it has been suggested[43] that this equivalence is caused by the presence of two valence tautomers,(28) and (29), which interconvert rapidly on the nmr time scale, resulting in time-averaged C_{2v} symmetry. Variable temperature ^{1}H nmr spectroscopic studies[39,44,45] have shown that there is no

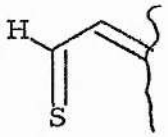
(28) (29)

departure from C_{2v} symmetry at temperatures down to -60°C. This cannot be regarded as conclusive evidence for time-independent symmetry, as tautomers (28) and (29) may still interconvert rapidly at low temperatures, giving a time-averaged signal.

Reid and co-workers[37] have compared the chemical shift of the 2-H protons in 1, 6, 6aλ^4-trithiapentalenes with the chemical shift of the thioformyl proton in stable heterocyclic thioaldehydes[46,47]. The thioformyl proton does not resonate at higher field than δ 10.2, even when the thioaldehyde is highly polarised in the sense $R\overset{+}{=}CH\text{-}S^{-}$. The chemical shifts of the 2-H protons in trithiapentalenes generally occur in the region δ 8.5-9.4. Although this is consistent with environment (30) rather than (31), the resonance at δ 8.5-9.4 could be the average of two signals.



(30)



(31)

Chemical shift values for the ring protons in triheteropentalenes suggest the presence of a ring current, due to π-electron delocalisation. Figure (1) shows that deshielding

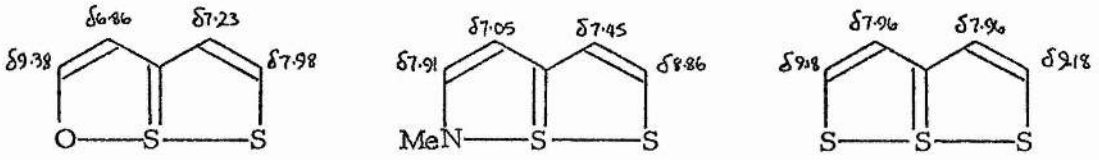


Figure (1). Chemical shifts (ppm) in triheterapentalenes.

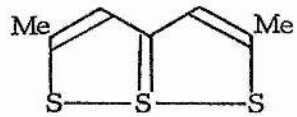
increases from oxa-[48] to aza-[49] to thia-[37] analogue. Lozac'h[50]

has estimated that the ring current in 2,5-dimethyl-1,6,6aλ^4-trithiapentalene (2) is about 65% of that in naphthalene.

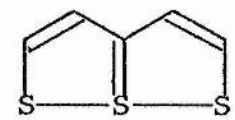
^{13}C nmr studies[51,52] support the theory that symmetrically substituted trithiapentalenes have C_{2v} symmetry in solution. Carbons (2) and (5), and (3) and (4) are equivalent. Again, the possibility that this equivalence is caused by time averaging of two different signals cannot be discounted.

3. Miscellaneous Spectroscopic Techniques

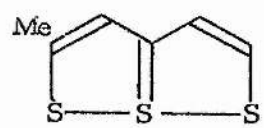
Clark and co-workers[53,54] have studied various trithiapentalenes in the solid state, using X-ray photoelectron spectroscopy to measure the sulphur molecular core binding energies. The values obtained for 2,5-dimethyl-1,6,6aλ^4-trithiapentalene (2) and 1,6,6aλ^4-trithiapentalene (1) indicate that there are two types of sulphur present in each compound, in a 2:1 ratio, and therefore that these compounds possess symmetrical structures. In contrast, the sulphur molecular core binding energies for trithiapentalenes (7) and (9) indicate the presence of three types



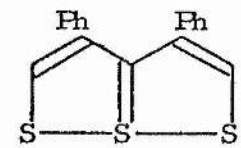
(2)



(1)



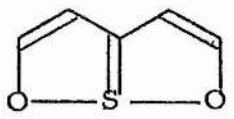
(9)



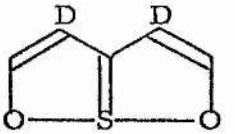
(7)

of sulphur in these two compounds. Hence both compounds are unsymmetrical in structure. Clark's results are in agreement with X-ray crystallographic data, which suggests symmetrical structures for compounds (1)[7] and (2)[11-13], and unsymmetrical structures for compounds (7)[18] and (9)[20]. However, the results of a similar study by Lindberg[55] imply that 2,5-dimethyl-1,6,6aλ^4-trithiapentalene (2) has an unsymmetrical structure.

Pedersen has recorded the microwave spectrum of 1,6-dioxa-6aλ^4-thiapentalene (32)[56], and its 3,4-dideutero derivative (33). The rotational transitions observed in various different vibrational states enabled several modes of vibration of the



(32)



(33)

molecules to be assigned. The results were consistent with C_{2v} symmetry.

In general, infrared and ultraviolet spectroscopy are of little value in determining the structure of triheterapentalenes.

B. BONDING IN 1,6,6aλ^4-TRIHETERAPENTALENES

Any acceptable description of the bonding in 1,6,6aλ^4-triheterapentalenes must explain the unique features of these systems, namely, the approximate collinearity of the three heteroatoms, the planarity of the molecules, and the inter-heteroatomic distances which indicate a bond order of less than unity.

Several theories have been propounded[11,54,57-70] concerning the bonding in such compounds, and have met with varying degrees of success. One describes 1,6,6aλ^4-trithiapentalenes as 'single bond-no bond resonance' compounds[11,57-59]; another represents them as having sulphonium ylid structures[60]. Other proposals require valence shell expansion of the central heteroatom to allow its d-orbitals to participate in σ-bonding[61-64].

The involvement of d-orbitals in the bonding of 1,6,6aλ^4-trithiapentalene was, for several years, a contentious issue[70]. Hordvik _et al_[66] included d-orbitals in their CNDO/2 calculations of substituent effects, obtaining results consistent with experimental observations. Early Extended Hückel Calculations[65] showed that closest correlation with observed results was achieved when d-orbitals were utilised.

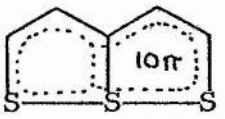
Recently more sophisticated calculations[54,67-69], using _ab initio_ and CNDO methods have refuted this. Clark[54], and

Palmer and Findlay[68] have independently compared the ground state energies of 1,6,6aλ^4-trithiapentalenes, both including and neglecting 3d-orbitals. They conclude that d-orbital participation on sulphur is not important, both in 1,6,6aλ^4-trithiapentalenes, and in other triheterapentalenes.

Today, the most widely accepted[3-6] theory of bonding in 1,6,6aλ^4-trithiapentalenes is that of Gleiter and Hoffmann[65]. This proposes that the three sulphur atoms of a 1,6,6aλ^4-trithiapentalene are held together by a four-electron three-centre bond. Three atomic p-orbitals, one from each of the sulphur atoms, are combined to form three molecular orbitals, one of which is bonding, one nonbonding and one antibonding. The electron density of the doubly occupied bonding molecular orbital is delocalised over all three centres, whereas the nonbonding orbital, also doubly occupied, has its charge localised mainly on the lateral atoms. The antibonding orbital remains vacant. Thus, to a first approximation, the three centres are held together by two electrons. This is consistent with the unusually long S-S bond lengths observed (see Section A). Additionally, 1,6,6aλ^4-trithiapentalenes possess 10π-electron systems. Each carbon atom, and the central sulphur atom provide one electron, and the two lateral sulphur atoms each contribute a pair of electrons to the π-system. The stabilisation of the three-centre bond by this π-bonding system is expected to be slight, as the equilibrium distance for the three-centre bond is reached at a stage where pπ-pπ overlap is small. Thus the 1,6,6aλ^4-trithiapentalene system may be

represented by formula (34) or (35). Gleiter and Hoffmann's

(34)



(35)

theory can be used to explain the bonding in all triheterapentalenes synthesised to date.

The concept of electron-rich three-centre bonding is well known[71,72] in inorganic chemistry, eg. Br_3^- [73,74], I_3^- [75,76], $(SeCN)_3^-$ [77,78], exhibit this phenomenon. In the linear triiodide ion, the three iodine atoms have bond lengths which are approximately 9% longer than the I-I distance found in molecular iodine[75,76]. 1,6,6aλ^4-Trithiapentalenes show a roughly equivalent degree of bond lengthening, in comparison with the normal S-S distances (see Section A).

C. SYNTHESIS OF 1,6,6aλ^4-TRIHETERAPENTALENES

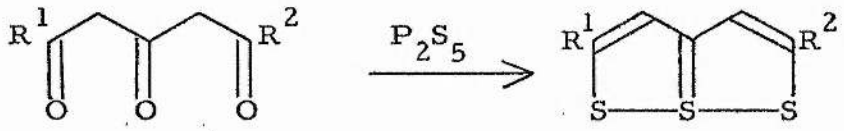
The work described in this thesis is concerned with the synthesis of nitrogen-containing triheterapentalenes. The more important synthetic routes to these compounds are summarised here.

Azapentalenes are frequently prepared from trithiapentalenes. The most convenient general syntheses of trithiapentalenes are therefore included in this section.

1. Synthesis of 1,6,6aλ^4-Trithiapentalenes

a. From 1,3,5-Triones

1,3,5-Triones (36) react with phosphorus pentasulphide to give trithiapentalenes (37) directly. Many 2,5-disubstituted

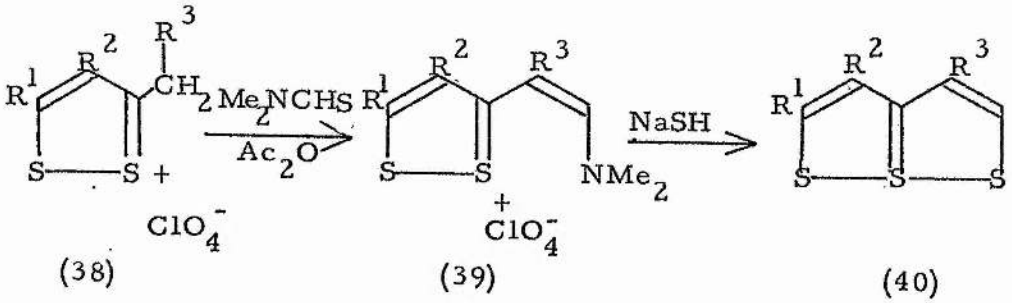


(36) (37)

1,6,6aλ^4-trithiapentalenes have been prepared using this method[79-83]. Yields are variable.

b. From 1,2-Dithiolium Salts

The 3-methyl(ene) group in 1,2-dithiolium salts (38) is acidic[84], and condenses with dimethylthioformamide in boiling acetic anhydride to form the Vilsmeier salts (39).

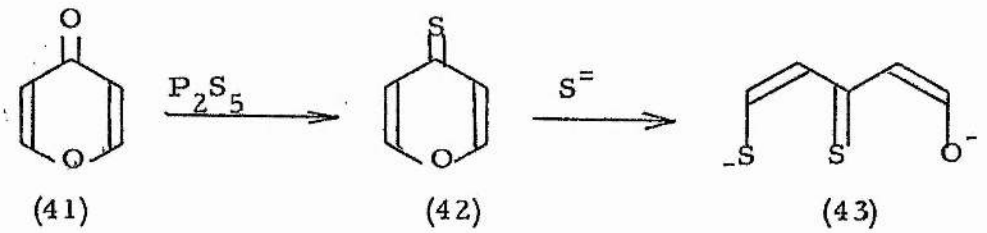


(38) (39) (40)

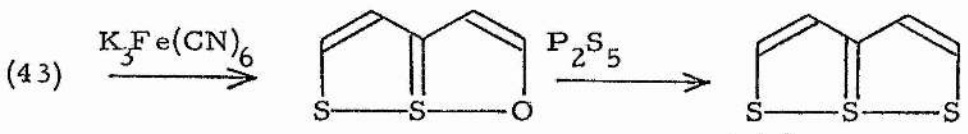
Trithiapentalenes (40) are obtained by treating these salts with sodium hydrogen sulphide[37].

c. From γ-Pyrone and Related Compounds

Reid[48] has synthesised 1, 6, 6aλ^4-trithiapentalene (45) from γ-pyrone (41). Thionation of compound (41) gave 4H-pyran-4-thione (42). This was ring-opened with sulphide



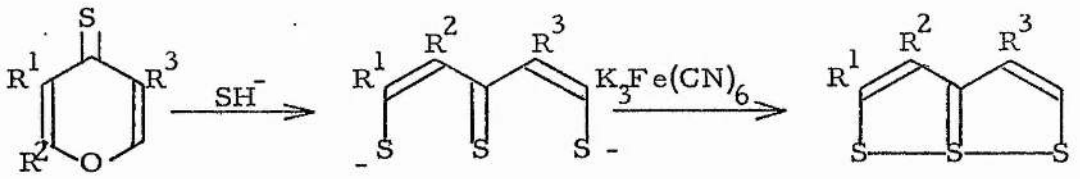
(41) (42) (43)



(44) (45)

ion and the resulting anion (43) was coupled oxidatively with potassium ferricyanide, producing the oxadithiapentalene (44). Subsequent thionation of compound (44) with phosphorus pentasulphide gave the trithiapentalene (45).

4H-Thiopyran-4-thiones (46) undergo similar ring-opening and intramolecular oxidative coupling reactions[85] (see Scheme 1).



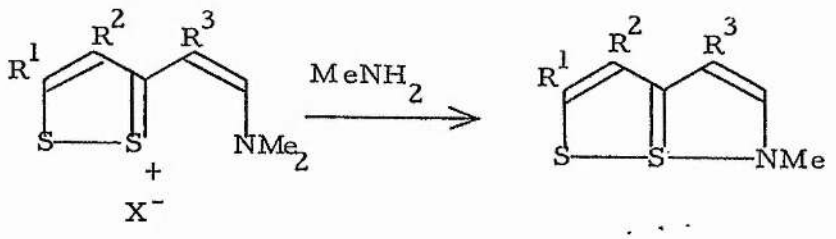
(46)

Scheme 1

2. Synthesis of Nitrogen-Containing 1, 6, 6aλ^4-Triheterapentalenes

a. Triheterapentalenes Containing One Nitrogen Atom

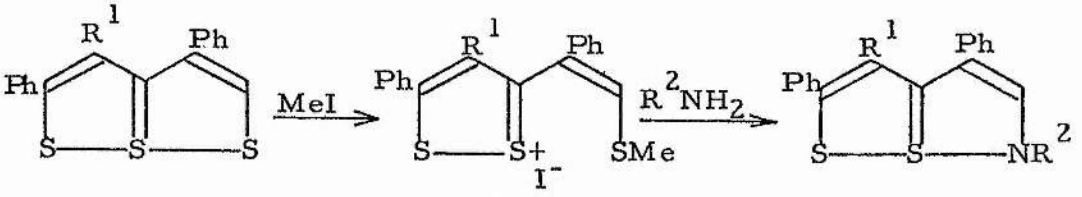
1, 6aλ^4-Dithia-6-azapentalenes (47) are conveniently synthesised[49, 86] by treating the Vilsmeier salts (39) with



(39) (47)

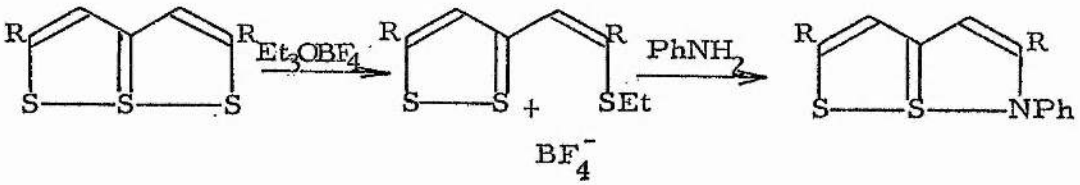
methylamine. Trithiapentalenes (48, R^1=H, Ph) react with methyl iodide, forming dithiolium salts (49). Treatment of

these salts with primary amines gives compounds (50)[87].



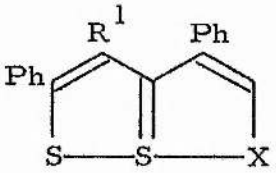
(48) (49) (50)

Reaction of trithiapentalenes (48) with sulphur dichloride gave intermediates which were not characterised, but on treatment with aniline they yielded compounds (50, R^2=Ph)[87]. Trithiapentalenes (37) are less reactive towards methyl iodide than trithiapentalenes (48), and are S-ethylated by the more powerful alkylating agent triethyloxonium fluoroborate[44]. The



(37) (51) (52)

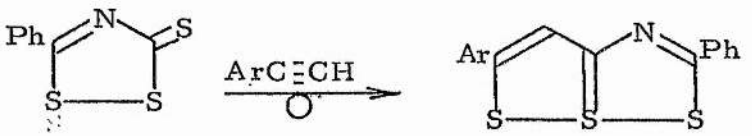
resulting salts (51) react with aniline to give the 1, 6aλ^4-dithia-6-azapentalenes (52). Compounds (53, X=O,S) react directly



(53)

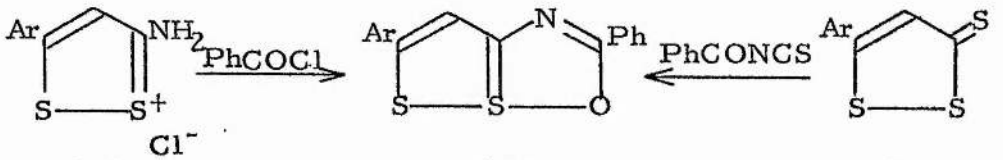
with primary amines, forming 1, 6aλ^4-dithia-6-azapentalenes (50)[59, 87].

Acetylenes react with 1, 2, 4-dithiazole-3-thione (54) with rearrangement, to give aza compounds (55)[88].



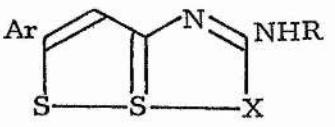
(54) (55)

The reaction of 1, 2-dithiolium salts (56) with benzoyl chloride or 1, 2-dithiole-3-thiones (57) with benzoyl isothiocyanate gives



(56) (58) (57)

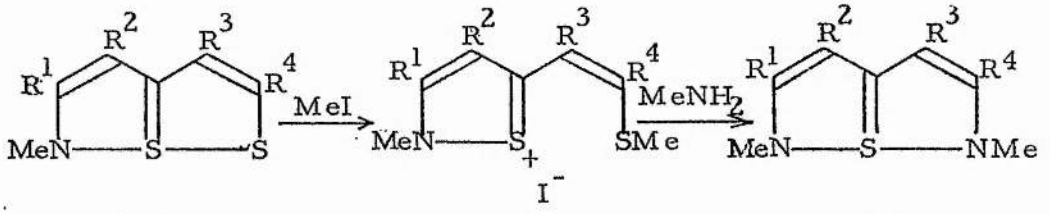
rise to the products (58)[88, 89]. Thionation of compounds (58) gives 1, 6, 6aλ^4-trithia-3-azapentalenes (55). The salts (56) react with iso(thio)cyanates[88] forming compounds (59, X=O, S).



(59)

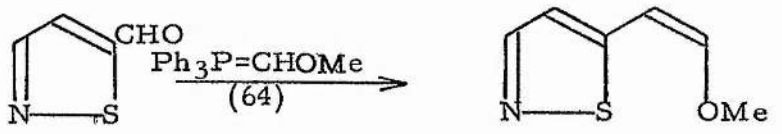
b. Triheterapentalenes Containing Two Nitrogen Atoms

Isothiazolium salts (61), formed by the treatment of 1, 6aλ^4-dithia-6-azapentalenes (60) with methyl iodide, react with methylamine to give 6aλ^4-thia-1, 6-diazapentalenes (62)[39].

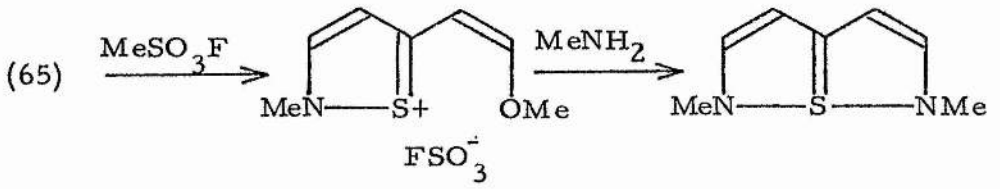


(60) (61) (62)

5-Formylisothiazole (63) reacts with the phosphonium ylid (64) in a Wittig reaction to give compound (65). N-Methylation of this compound with methyl fluorosulphonate followed by reaction with aqueous methylamine, gives the thiadiazapentalene (66)[90].

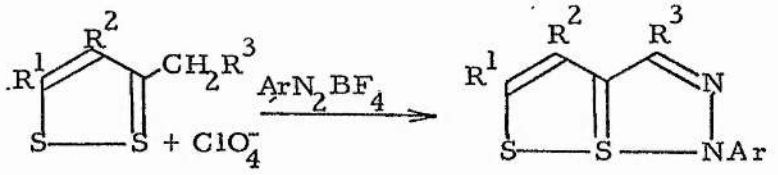


(63) (65) cis and trans



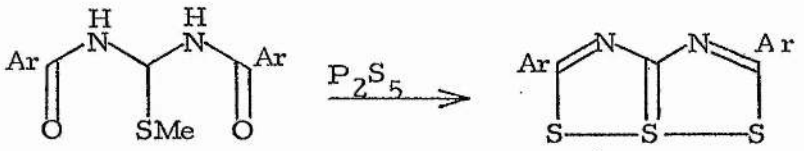
cis and trans (66)

1, 2-Dithiolium salts (38) react with arenediazonium fluoroborates to give 6, 6aλ^4-dithia-1, 2-diazapentalenes (67)[91].



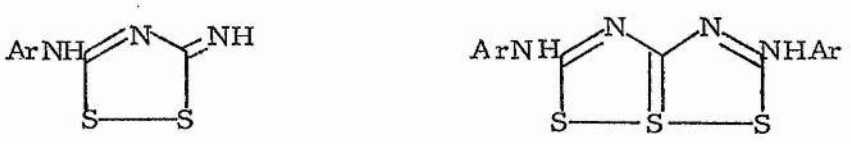
(38) (67)

1, 6, 6aλ^4-Trithia-3, 4-diazapentalenes (69) have been synthesised by thionating N, N'-diaroyl-S-methylisothioureas (68) with phosphorus pentasulphide[92, 93]. Thionation of N, N'-diaroyl ureas was less successful. Behringer[94] found



(68) (69)

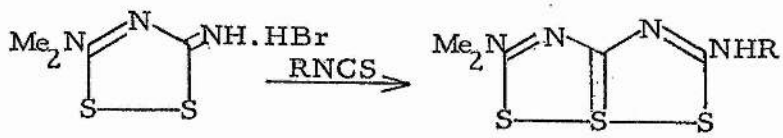
that arylisothiocyanates reacted with compound (70). On being heated, the 3, 4-diaza analogues (71) were obtained.



(70) (71)

Oliver[95] synthesised similar compounds (73), by allowing the

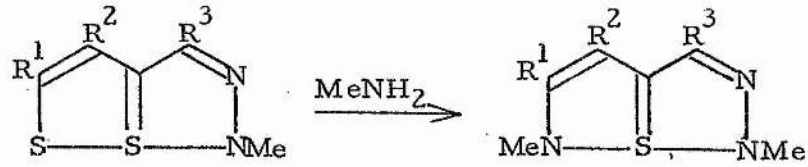
salt (72) to react with isothiocyanates.



(72) (73)

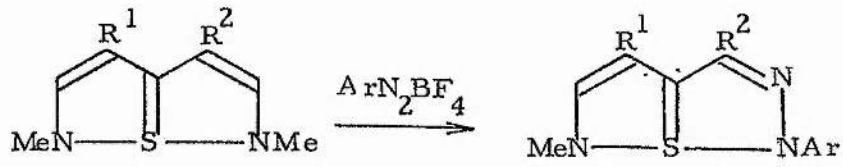
c. Triheterapentalenes Containing Three Nitrogen Atoms

6aλ^4-Thia-1,2,6-triazapentalenes (74) are formed directly[96] by the action of methylamine on 6,6aλ^4-dithia-1,2-diazapentalenes (67).



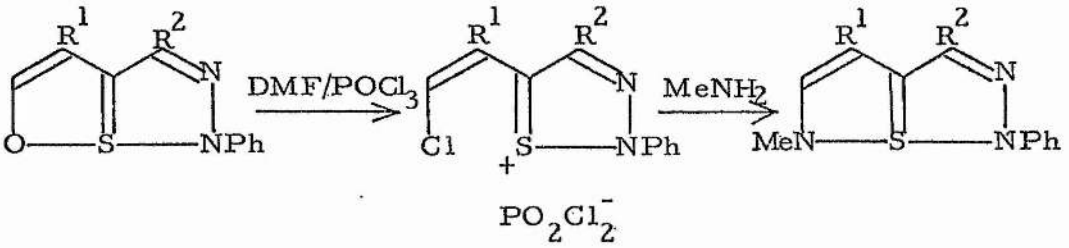
(67) (74)

In a new synthesis[96], 1,6-diaza compounds (75) coupled with arenediazonium fluoroborates to form the 1,2,6-triaza compounds (76). A methyliminomethyl group was eliminated during this reaction.

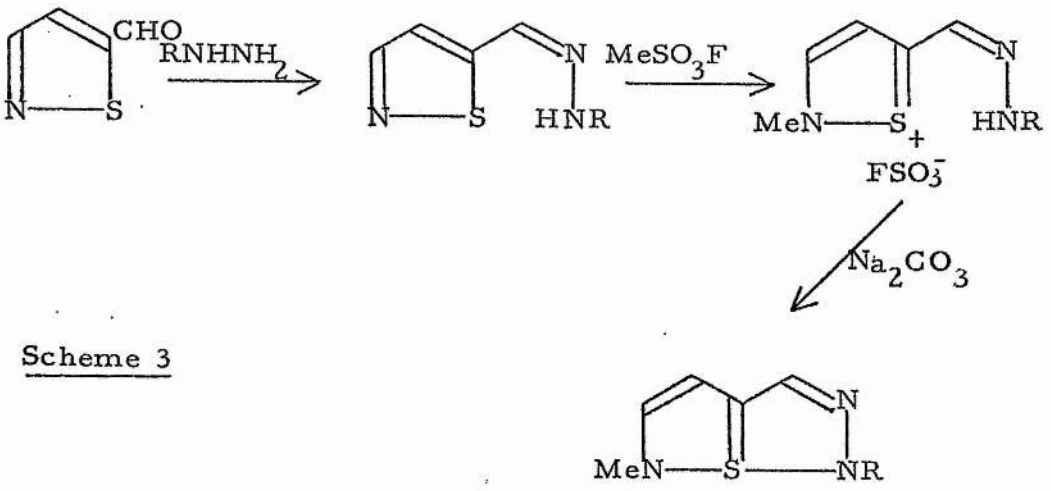


(75) (76)

Reid and Czyzewski[90] have recently developed syntheses of 6aλ^4-thia-1,2,6-triazapentalenes from oxathiadiazapentalenes (see Scheme 2) and from 5-formylisothiazole (Scheme 3).



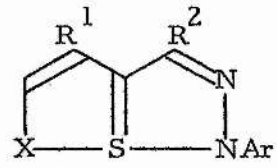
Scheme 2



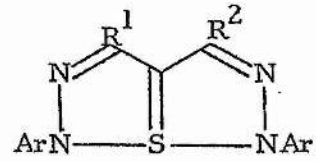
Scheme 3

d. Triheterapentalenes Containing Four Nitrogen Atoms

6aλ^4-Thia-1,2,5,6-tetraazapentalenes (78) have been recently prepared[41,96] by treating compounds (77; X=O, NMe) with arenediazonium tetrafluoroborates.

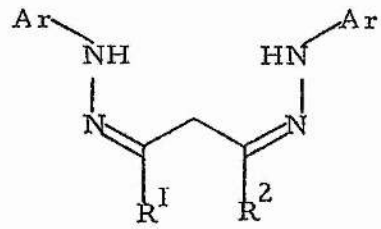


(77)



(78)

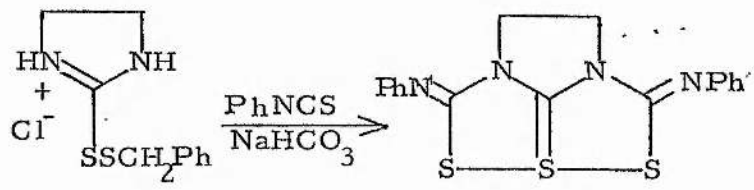
A new synthesis by Vialle[97] uses bis-phenylhydrazones (70), which, when treated with sulphur di- or monochloride, produce tetraazapentalenes (78).



(79)

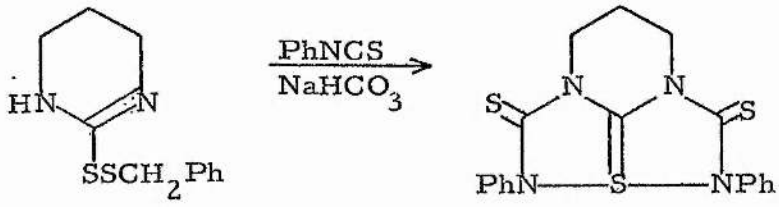
e. Triheterapentalenes Containing Exocyclic Double Bonds

An X-ray crystal structure determination[98] of the adduct of compound (80) with phenylisothiocyanate[99] has shown that the product is the trithiadiazapentalene derivative (81).



(80) (81)

When the method used for the preparation of compound (81) was applied to the disulphide (82), compound (83) was obtained[99].



(82) (83)

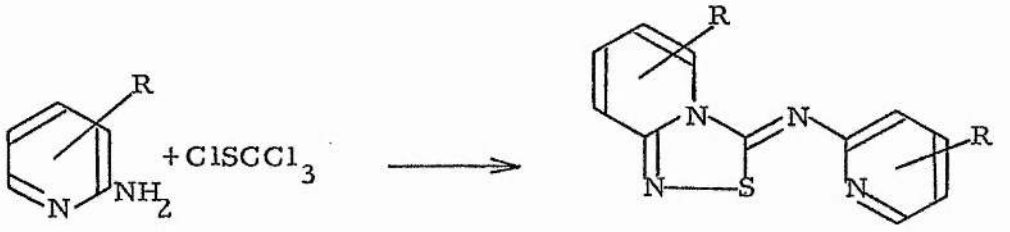
Compounds (81) and (83) are novel in that they are examples of triheterapentalenes containing exocyclic double bonds. They have been described as derivatives of a hypothetical tetrahydro-1, 6, 6aλ^4-triheterapentalene[6].

D. ANALOGUES OF 1,6,6aλ^4-TRIHETERAPENTALENES BASED ON THE 1,2,4-THIADIAZOLE SYSTEM

A number of compounds which have been described in the literature as 1,2,4-thiadiazoles may be reformulated as triheterapentalenes. This section describes the preparation of these compounds.

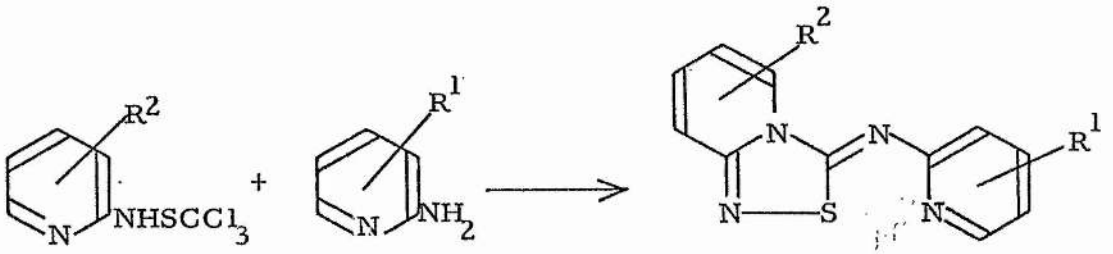
1. 3-(2-Pyridylimino)-3H-[1,2,4]Thiadiazolo[4,3-a]Pyridines and Related Compounds

Potts and Armbruster[100] have prepared a series of compounds which they formulated as 3-(2-pyridylimino)-3H-[1,2,4]thiadiazolo[4,3-a]pyridines (85), by treating substituted 2-aminopyridines (84) with perchloromethyl mercaptan, in the



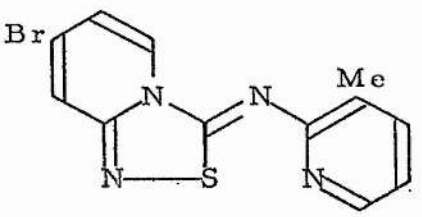
(84) (85)

presence of base. The scope of this synthesis was extended[101] by allowing the intermediate (86)[102] to react with other 2-aminopyridines (87). The products (88) may be reformulated

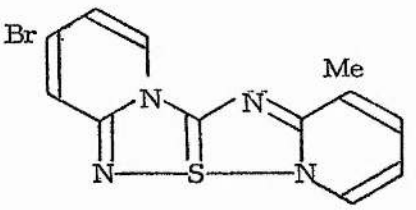


(86) (87) (88)

as triheterapentalene-type structures, eg. (89) is reformulated as (90).



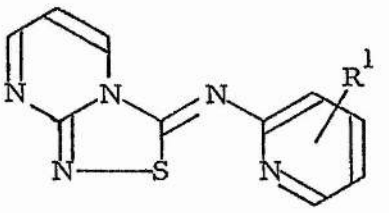
(89)



(90)

2-Aminopyrimidine reacted with perchloromethyl mercaptan, to give the intermediate (91), which subsequently reacted with

(91)



(92)

2-aminopyridines, to form the products (92)[103]. However, compound (94), prepared from 3-amino-5-methylisoxazole (93)

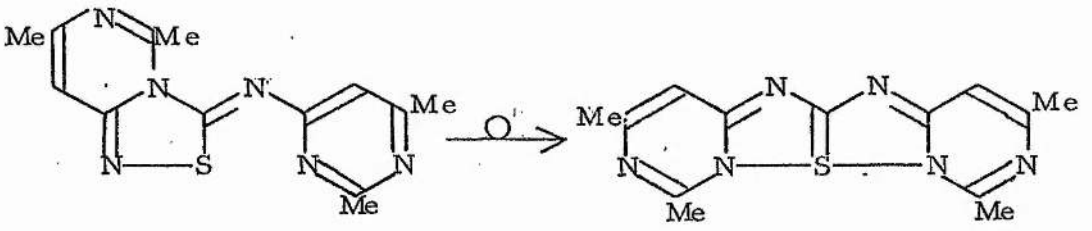
in a similar reaction, failed to give the desired products,

(93)

(94)

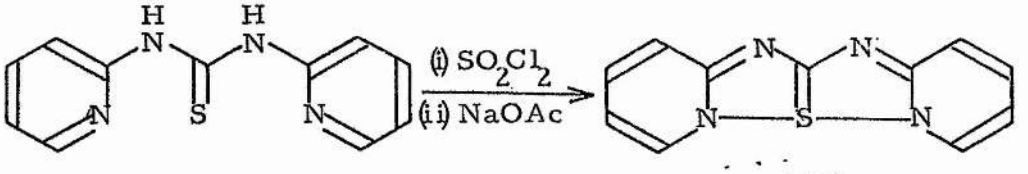
on treatment with 2-aminopyridines [104].

Compound (95) underwent a Dimroth rearrangement[105], on treatment with dilute sodium hydroxide followed by phosphoryl



(95) (96)

chloride, to the product (96). Potts formulated this compound as the triheterapentalene (96), because the ^{1}H nmr spectrum showed only two signals for the four methyl groups. Harris[106] had previously synthesised a similar compound (97) (see Scheme 4). He too represented his product as a triheterapentalene.

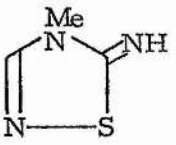


(97)

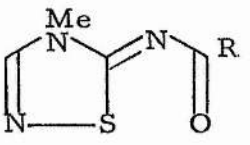
Scheme 4

2. 5-Imino-1,2,4-Thiadiazole Derivatives

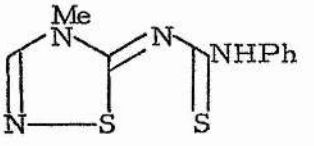
Goerdeler and coworkers[107-109] synthesised several derivatives of the 1,2,4-thiadiazole (98). Acylation[107] resulted in the formation of products formulated as (99, R=Me, Ph, EtO) while the reaction with phenyl isothiocyanate in petroleum[107] gave a compound formulated as (100).



(98)

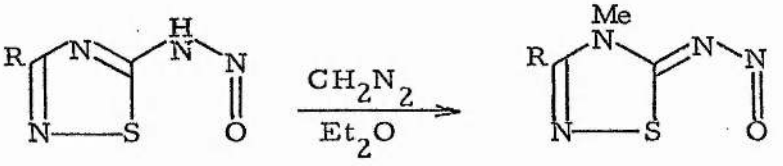


(99)



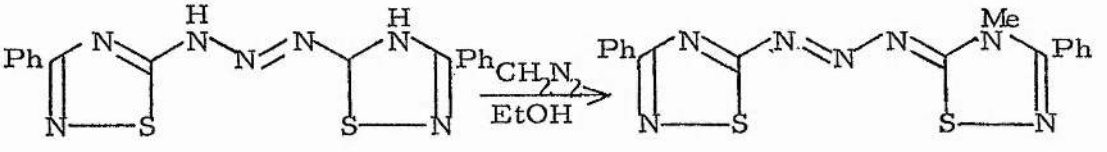
(100)

Nitrosation[107] with sodium nitrite in dilute hydrochloric acid gave products described as nitroso compounds (102, R=H). The action of diazomethane[108] on 5-nitrosamino-1,2,4-thiadiazoles (101, R=Ph, $PhCH_2$) served as an alternative route to compounds



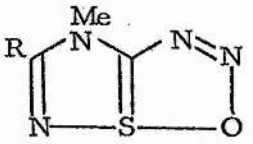
(101) (102)

of this type. Diazomethane reacted with an alcoholic solution of triazine (103)[109] producing the triazine (104) as a minor product.



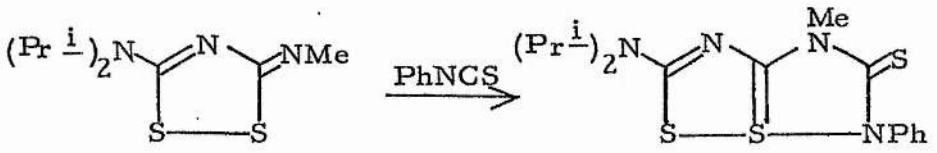
(103) (104)

The foregoing products can alternatively be represented as bicyclic species, eg. (102) can be reformulated as (105).



(105)

An X-ray crystal structure determination[110] of the adduct of compound (106) with phenyl isothiocyanate[111] has shown

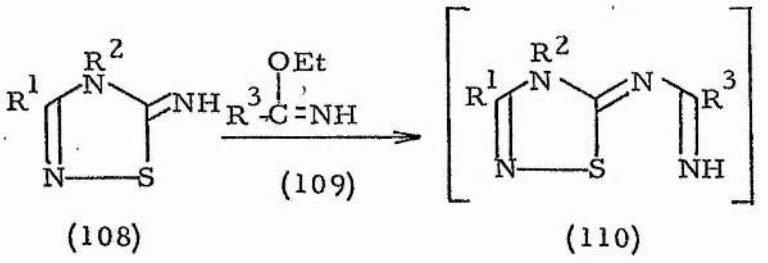


(106) (107)

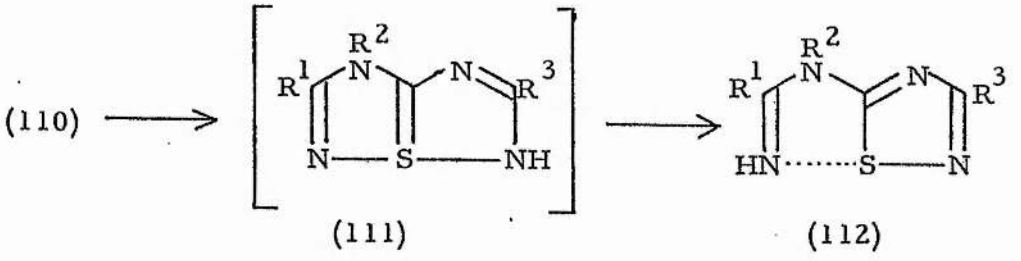
the compound to be the 1,6aλ^4-dithia-6-azapentalene derivative (107).

3. Rearrangements Involving Triheterapentalene Intermediates

Akiba has studied the reaction of the imines (108) with imidates (109)[112]. The expected product (110) was not isolated. X-Ray structural analysis of the product, where $R^1=R^2=R^3=Me$ showed that compound (112) was obtained. Akiba explained this result in terms of a bond-switch rearrangement. He postulated that the expected product (110) was formed, then rearranged to give compound (112), via the triheterapentalene-type intermediate (111). In this type of rearrangement, the sulphur atom from the original heterocyclic ring is incorporated into the newly-formed ring.

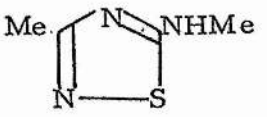


(108) (109) (110)



(110) (111) (112)

However, Goerdeler has shown[113] that the imine (108, $R^1=R^2=Me$) rearranges, albeit on prolonged heating and in low yield, to give compound (113). Reaction of compound (113) with imidate is known[112] to result in the formation of compound (112),

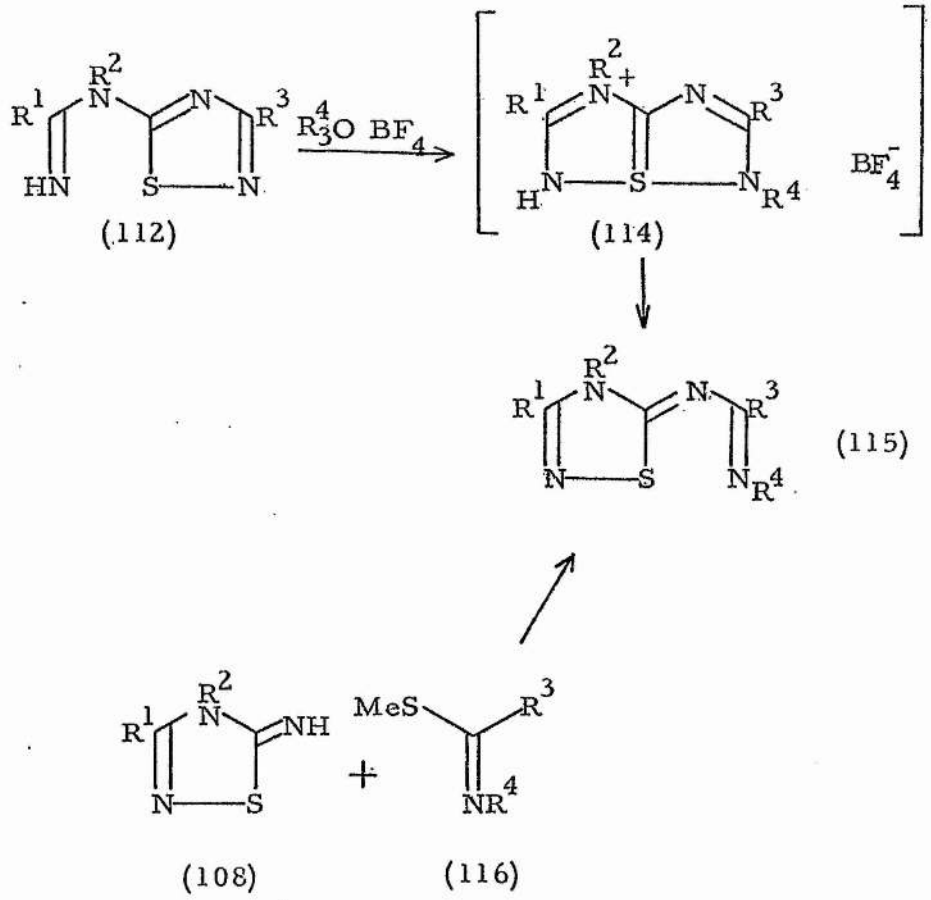


(113)

without a bond switch taking place. The validity of the crystal structure determination of compound (112, $R^1=R^2=R^3=Me$) and therefore the bond switch theory are both open to question, in this case.

The X-ray crystal structure determination of compound (112, $R^1=R^2=R^3=Me$) shows that the molecule is approximately planar, with S-N and S-NH distances of 1.668 Å and 2.500 Å respectively. Akiba regarded this planarity and the HN-S separation as indicative of an intramolecular N····S interaction, which he represented by a dotted line. However, Glemser et al[114] have presented a correlation of S-N distance with S-N bond order, which suggests that the S-N bond order becomes zero at an interatomic distance of ca. 2.0 Å. If this correlation is valid there are no grounds for suggesting that there is any significant S····N bonding interaction in compound (112).

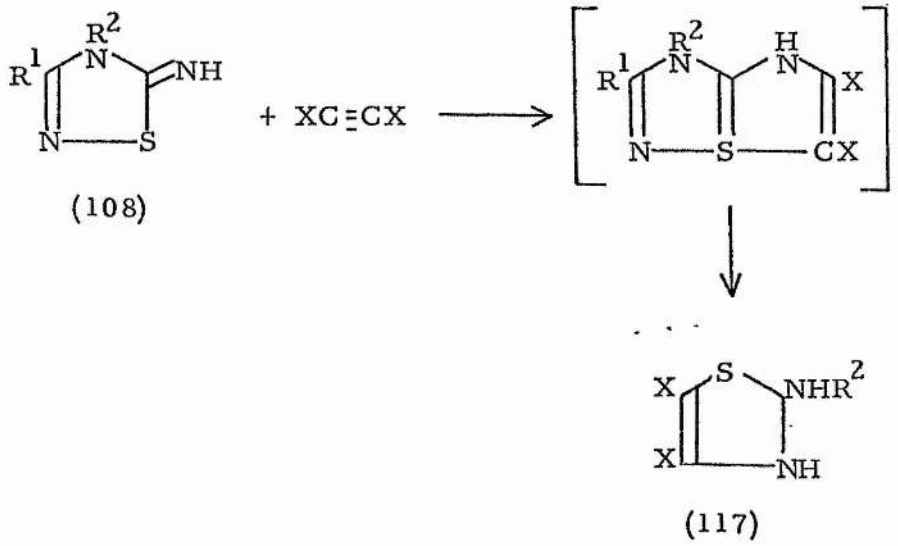
Akiba has found other examples of bond switch rearrangements[115], including the reaction of compound (112) with Meerwein's reagent, via the proposed intermediate (114), to give compound (115). The structure of compound (115) was confirmed by an unequivocal synthesis from compounds (108) and (116).



(112) (114) (115)

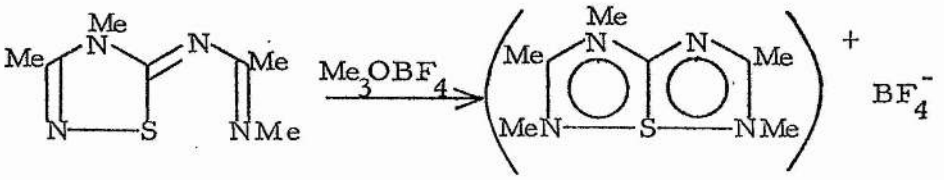
(108) (116)

The reaction of the imines (108) with activated acetylenes apparently involves a bond switch[116]. No details have been given as to how the structure of the product (117) was established.



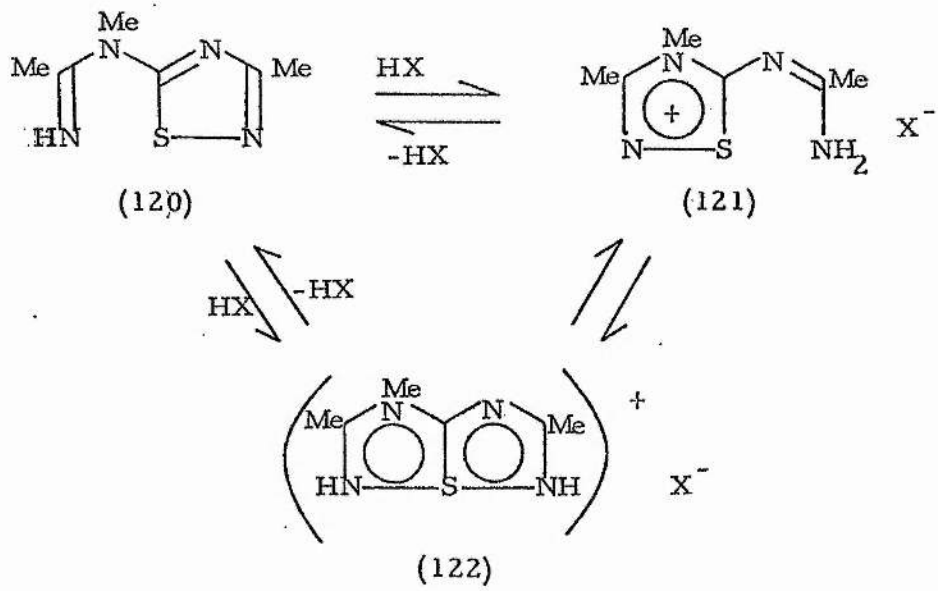
(108) (117)

Akiba allowed compound (118) to react with Meerwein's reagent, giving a product formulated as (119)[116]. X-Ray crystallography has shown that the N-S bond lengths are 1.984 Å and 1.833 Å. No further details have been published. The compound may therefore be regarded as a triheterapentalenium salt.



(118) (119)

Akiba has claimed that the bases (120) form salts (121) via bond switching[115]. This claim is based on rather limited ^{1}H nmr spectroscopic evidence, which shows that the NH proton couples with the methyl group on the adjacent carbon, and that three of the methyl groups in salt (121), its N-methyl and N,N-dimethyl derivatives have very similar δ values. The ultraviolet spectrum of salt (121) shows a red shift and hyperchromism, compared with base (120). Akiba believes that this clearly demonstrates the presence of a salt containing a thiadiazolium ion. Addition of a half molar amount of trifluoroacetic acid (TFA) to base (120) in $CDCl_3$/DMSO-D_6 gave only three methyl signals. A linear relationship was observed between the chemical shift of one of the methyl groups, and the amount of TFA added. These facts



(120) (121) (122)

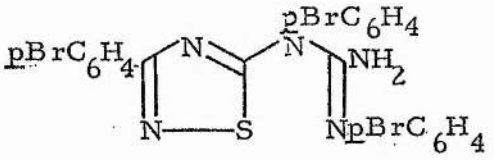
suggested that compounds (120) and (121) were equilibrating rapidly. On the basis of this information alone, Akiba proposed the formation of intermediate (122). He assumed that the N-S-N distances in compounds (122) and (119) were equivalent, and used this information to draw further conclusions. These are invalid, as his assumption about the bond lengths is totally without justification. It must also be noted that attempts to prepare triheterapentalenes containing the -NH unit in the 3-centre bonded sequence have, to date, proved unsuccessful[117].

Akiba reported[118] that the reaction products of Hector's bases, formulated as (123), with aryl cyanamides were the triheterapentalene derivatives (124). He drew this conclusion mainly on

(123) (124)

the rather weak basis of ultraviolet and infrared spectral comparisons with other heterocyclic systems, and from the mass spectra of compounds (124). Similar compounds were apparently obtained as byproducts in other reactions of Hector's bases[119].

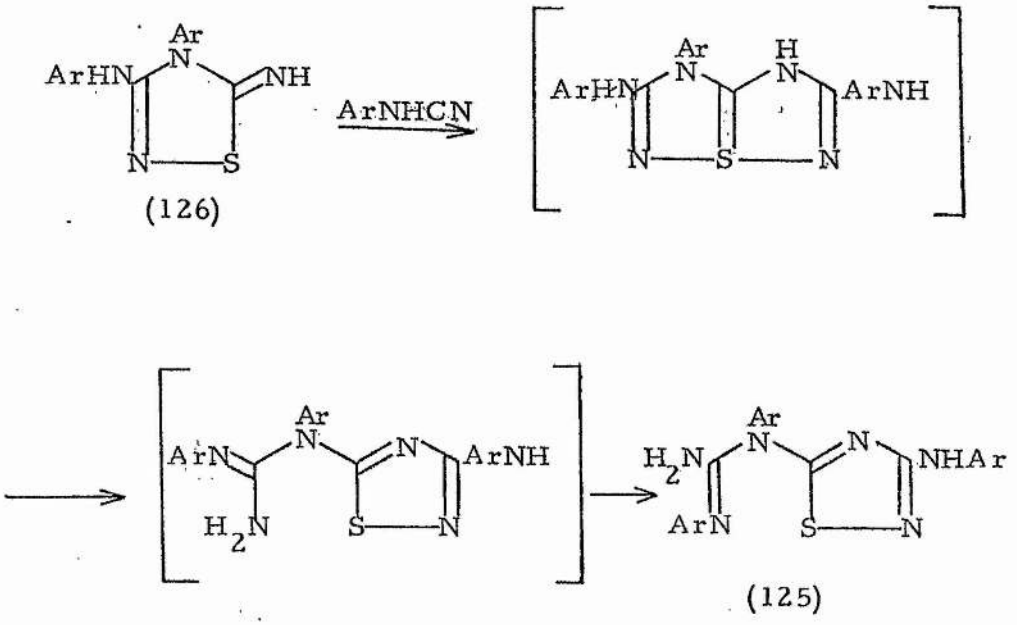
An X-ray crystal structure determination[120] of product (124, Ar=pBrPh) has shown that the correct structure is (125).



(125)

The molecule is approximately planar, with S-N distances of 1.670 Å and 2.538 Å. Akiba considers[120] that these interatomic distances constitute evidence of significant S····N intramolecular interaction. This is without foundation. He also stated that product (125) must have arisen from a bond switch rearrangement, followed by prototropy.

Recently, Hector's base has been shown[121] to have structure (126), rather than structure (123), favoured by Akiba. Its structure is identical in the solid state[121], and in solution[122]. Therefore the formation of product (125) may be explained in terms of a bond switch, followed by prototropy, and subsequent bond rotation (see Scheme 5).

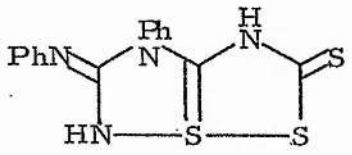


(126)

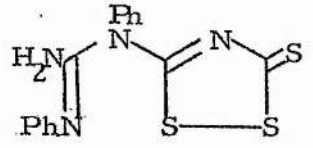
(125)

Scheme 5

The carbon disulphide adduct of Hector's base is known[123]. Butler[124] recently proposed a structure for this compound, formulating it as containing a hypervalent sulphur atom (127).



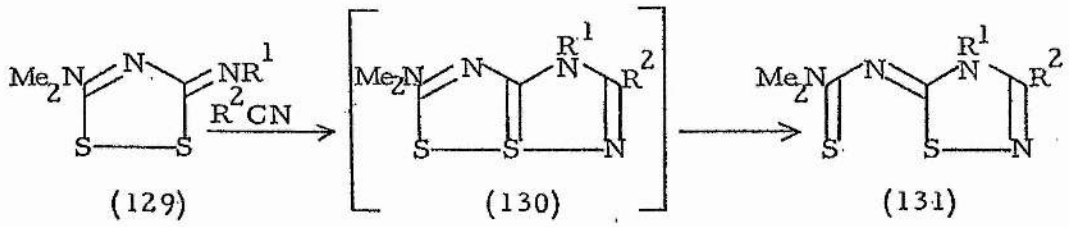
(127)



(128)

However, Glidewell[124] has shown the correct structure to be (128). This rearrangement clearly involves a bond switch.

Oliver[126] has found another example of a bond switch. The 2-iminodithiazole (129) reacted with nitriles to give a product formulated as the thiadiazole (131). A triheterapentalene-type



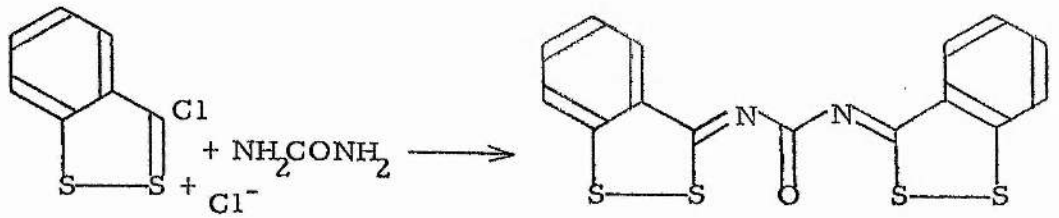
(129) (130) (131)

intermediate (130) was proposed.

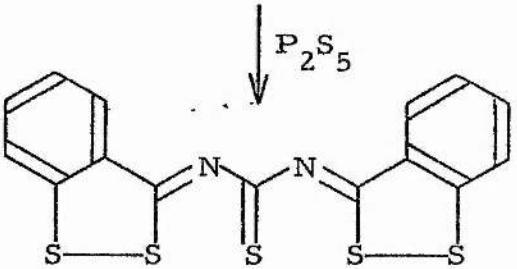
E. ORGANIC COMPOUNDS CONTAINING FIVE-CENTRE BONDS

The concept of n-centre bonding has been discussed by Carpenter[127], and Muller[128]. It was concluded that theoretically, when n $\geqslant 4$, the stability gained by the formation of an n-centre bond would not alone be sufficient to hold the atoms in favourable positions for bonding. Higher analogues of triheterapentalenes could exhibit n-centre bonding. The carbon skeleton of these molecules would help to hold the heteroatoms in the correct orientation for bonding.

Several compounds containing an array of five sulphur atoms have been synthesised. Klingsberg obtained compound (133), in a two step synthesis[129], from 3-chloro-4,5-benzo-1,2-dithiolium chloride (132) and urea, as follows:-

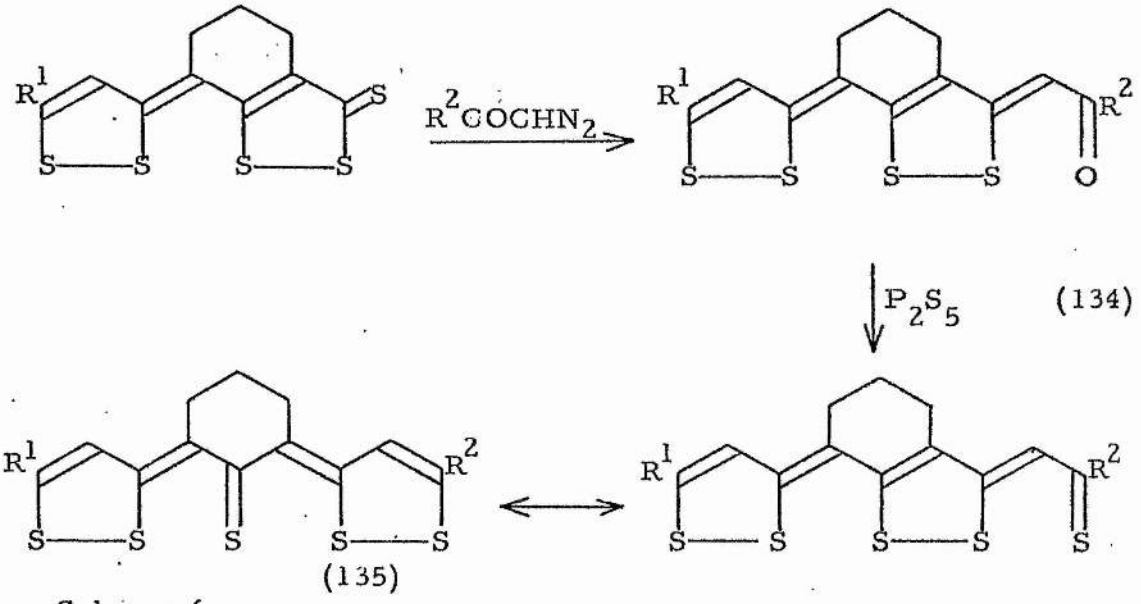


(132)



(133)

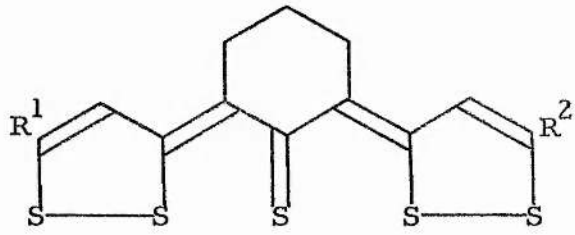
Stavaux and Lozac'h[130,131] synthesised compounds of type (135) using the reactions of Scheme 6. ^{1}H Nmr spectroscopy suggests



Scheme 6

that compound (135) has a symmetrical structure[131].

The structures of the three derivatives (135a)[132,133], (135b)[134] and (135c)[135] of compound (135) have been determined by X-ray crystallography. S-S Bond lengths are given below.



(135a)	2.183	2.580	2.583	2.173	$R^1=R^2=Bu^t$
(135b)	2.179	2.554	2.582	2.149	$R^1=Ph, R^2=Bu^t$
(135c)	2.113	2.626	2.396	2.271	$R^1=R^2=pMeC_6H_4$

Compound (135a) has twofold symmetry, within experimental error. The unsymmetrical species (135b) shows slight asymmetry, while the other symmetrically substituted compound (135c) deviates greatly from mirror-image symmetry.

The five sulphur atoms in compounds (135a), (135b) and (135c) are approximately collinear. Delocalised σ-bonding extending across all the sulphur atoms apparently exists. The S-S bonds seem to be very susceptible to weak interatomic forces. CNDO/2 calculations[136] predict that in compounds of type (135), all the S-S bonds will be longer than in dithioles, and that the outer S-S bonds will be shorter than the inner ones. Lengthening one of the outer S-S bonds should cause shortening of the other outer S-S bond. These calculations are in qualitative agreement with the experimental results.

Gleiter[137] has explained the inequalities of the S-S bond lengths, in terms of bond energies. The generation of an electron-rich multicentre bond, comprising a linear arrangement of sulphur centres, compensates approximately for the breaking of one S-S σ-bond. When a three-centre bond is formed, the rupture of one S-S single bond is nearly compensated for by the electron-rich three-centre bond. An electron-rich five-centre bond, however, must compensate for the breaking of two S-Sσ-bonds, which is energetically unfavourable. Therefore the structure does not have equal bond lengths between each sulphur atom.

A derivative of compound (134 , R^1=Bu^t, R^2=Ph) has been examined crystallographically[138]. It does not possess a delocalised σ-system which includes all the heteroatoms.

F. LUBRICATING OIL ADDITIVES

Several of the compounds synthesised during the course of this research project were tested for suitability as antioxidant additives in lubricating oils.

This section therefore serves as a brief introduction to the field of oil additives, with particular attention being paid to the use of triheterapentalenes and analogous heterocyclic compounds.

Lubricating oil additives are chemicals which are added to oils to enhance desirable properties, modify undesirable ones, or to create completely new properties. Concentrations of the additives may vary from a few p.p.m. to over 20%. The use of additives in oils has become widespread since World War II, principally in oils for internal combustion engines. The benefits which accrue have been so great that today an enormous range of additives is available, and most high performance lubricants contain several additives, each with a specific function[139]. However, the complexity of modern lubricant systems may bring problems, due to interaction and competition between the various additive components.

The main functions of the various types of additives can be summarised as follows:-

(i) Detergents, antioxidants and dispersants reduce the formation of engine deposits and sludge, formed by the operating conditions of the engine.

(ii) Basic detergents and antioxidants reduce corrosive wear,

by neutralising acids and other destructive byproducts.

(iii) Antiwear and extreme pressure agents reduce mechanical wear on heavily stressed engine components.

(iv) Viscosity index improvers and pour point depressants can modify oil properties, by controlling temperature-dependent fluidity, foaming, and by reducing the variation of viscosity with temperature.

Many modern additives can satisfy several of these requirements simultaneously. Further discussion in this thesis will be limited to antioxidants.

1. Antioxidants

In service, lubricants deteriorate through contamination and by physical and chemical changes due to oxidation. The oxidation products are principally acidic materials which corrode bearings, and asphaltenes, the polymeric compounds which form sludges and lacquers on metal surfaces. The adverse effects of these degradation products are minimised by the use of antioxidant additives.

Oxidation of mineral oil is a free radical chain reaction[140,141]. The primary product of this reaction is a peroxide, which rapidly decomposes at high temperatures to give more of the initiators which catalyse the chain reaction. Theoretically the oxidation can be controlled by stopping the chain sequence, using a chain inhibitor, or by destroying the peroxide with a peroxide decomposer.

In practice, mixtures of both types of inhibitors are most effective, as they combine to act synergistically[142]. Efficient peroxide destroyers are zinc dialkyldithiophosphates (ZDDP) and phospha-sulphurised terpenes, whereas chain inhibitors are commonly phenols or aromatic amines. Obviously, the presence of such bases will also neutralise any acid formed, thus assisting corrosion prevention.

Alternatively, oxidation may be discouraged by the formation of a protective acid-resistant film on the metal surface. ZDDP's, as well as being peroxide decomposers, are also thought to operate in this manner.

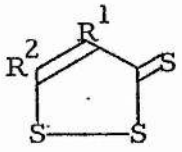
Unfortunately, oxidation cannot be prevented indefinitely, as the antioxidants themselves are eventually consumed.

2. Sulphur-Containing Heterocycles as Antioxidants

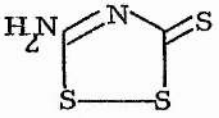
Recent concern over environmental pollution has instigated a search for new non-toxic organic lubricating oil additives. These are likely to be based on sulphur, nitrogen and oxygen, rather than phosphorus and the metals which the well-established additives contain.

The use of 1,2-dithiole-3-thiones as additives is well known. For example, early patents claimed aryl[143,144] and alkyl[145] derivatives of compound (136) as antioxidants. Compound (137) has been the subject of much work[146-148] in the fields of antioxidant and peroxide decomposition research. It has been claimed that

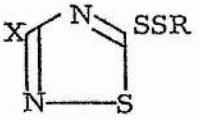
the 1,2,4-thiadiazoles (138, X=halogen, SSR) are corrosion inhibitors[149].



(136)

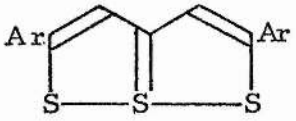


(137)

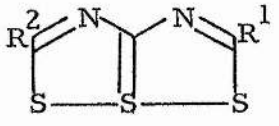


(138)

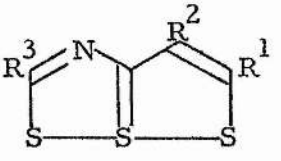
Interest has been shown in triheterapentalenes as lubricating oil additives, and 2,5-diaryl-1,6,6aλ^4-trithiapentalenes (139) have been used as antioxidants[150], as have the aza-analogues (37) and (140)[151]. Recently, a patent application has been filed[152] concerning the use of compounds (141) and (142, X=S, O) as antioxidants and bearing corrosion inhibitors.



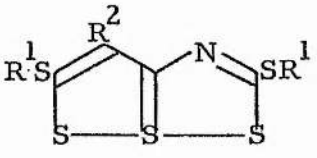
(139)



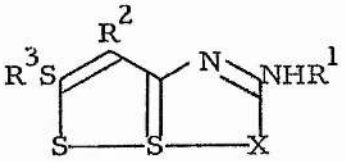
(37)



(140)



(141)



(142)

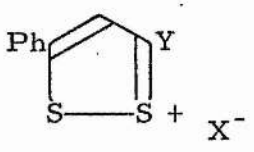
Compounds (37) and (139) to (142) are versatile and efficient additives compared with commercial antioxidants, proving effective at concentrations as low as 10 p.p.m.

DISCUSSION

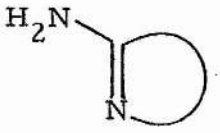
A. THE REACTION OF 3-SUBSTITUTED-5-PHENYL-1,2-DITHIOLIUM SALTS WITH HETEROCYCLIC AMINES

In the course of this work, the reaction between 1,2-dithiolium salts and various amino-heterocycles was investigated. This reaction is of particular interest as it can lead to a product which may be described as a triheterapentalene containing a pyridine-type nitrogen atom in the three-centre bonded sequence.

The 1,2-dithiolium salts (1) react with 2-aminoheterocycles, which are conveniently represented by formula (2). Two isomeric products may be formed in this reaction, and for each of these isomers more than one formulation is possible.



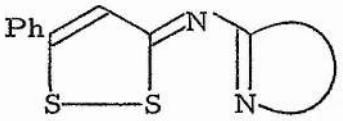
(1)



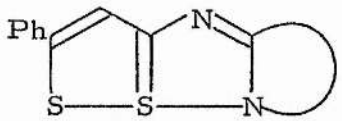
(2)

One isomer arises from condensation at the amino-nitrogen followed by elimination of HX and HY. The structure of this compound may be formulated in three different ways. The 3-imino-1,2-dithiole structure (3) is the most straightforward description of the product. However, the compound can also be formulated as the tricyclic species (4), an example of a

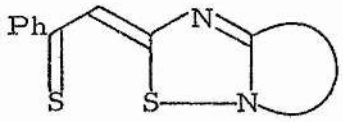
triheterapentalene fused to a heterocyclic ring. The third structural possibility is that of the thiocarbonyl compound (5).



(3)



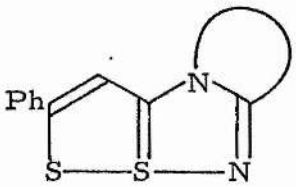
(4)



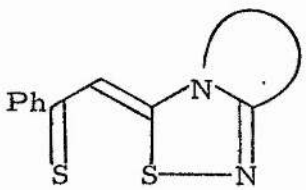
(5)

This type of structure would be formed in a rearrangement reaction, probably via an intermediate similar to compound (4), which would contain a hypervalent sulphur atom.

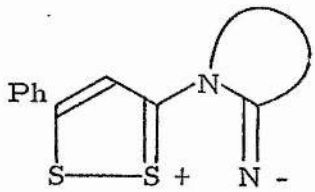
The other isomer results from attack at the heterocyclic nitrogen atom, with concomitant elimination of HX and HY. This product may be described as having the structure (6), (7), or (8).



(6)



(7)



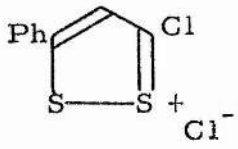
(8)

Structure (6) is an example of a triheterapentalene with a pyridine-type nitrogen incorporated into the three-centre bond. Hitherto, compounds of this type have been unknown. Existing triheterapentalenes possess a π-electron system, to which the lateral heteroatoms each contribute a pair of electrons. A pyridine-type nitrogen has only one electron available for π-bonding. The deficit would therefore be made up by the bridgehead nitrogen, which has the potential to donate two electrons for π-bonding. It

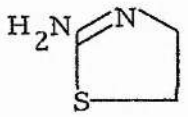
is possible that structure (6) might prove to be unstable, in which case rearrangement could lead to the thiocarbonyl species (7). It is rather unlikely that the compound would exist in the dipolar form (8), as the energy required to prevent a positive and a negative charge held in such close proximity from combining, would be very great.

1. The Reaction of 3-Substituted-5-phenyl-1,2-dithiolium Salts with 2-Amino-2-thiazoline

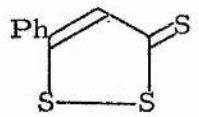
3-Chloro-5-phenyl-1,2-dithiolium chloride (9) reacted with 2-amino-2-thiazoline (10), in ethanol, to give four products which were separated by chromatography. The two major products were identified as 5-phenyl-1,2-dithiole-3-thione (11) and 5-phenyl-1,2-dithiole-3-one (12). These presumably arose from



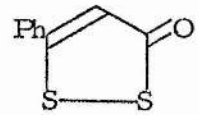
(9)



(10)



(11)

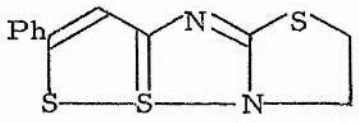


(12)

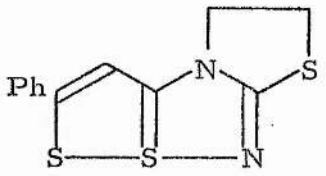
the breakdown of the dithiolium salt, before reaction with the amine could take place. Their presence was detected in every reaction of dithiolium salts which was studied.

A yellow and a more polar orange product were isolated as minor constituents of the reaction mixture. On the basis of the differing polarities of these materials, the yellow compound was

assigned structure (13), and the orange product structure (14). The yields were somewhat disappointing (see Table 1).



(13)



(14)

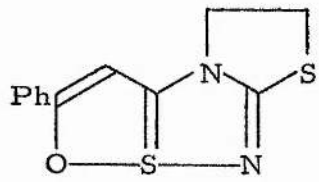
In an attempt to reduce the quantities of byproducts formed, and to increase the yields of compounds (13) and (14), the effect of using different solvents in the reaction was studied. Preliminary experiments indicated that methanol, benzene and dimethylformamide had no significant advantage over ethanol. The use of acetonitrile and hexamethylphosphoramide (HMPA) was investigated more thoroughly. The yields of products obtained with these solvents are shown in Table 1.

Table 1: Yields of Compounds (11)-(14) in Various Solvents

Solvent	Yield (%) of Compound			
	(11)	(12)	(13)	(14)
Ethanol	27	21	3.3	3.6
Acetonitrile	24	0	10.4	*
HMPA	15.5	*	0	2.8

* product impure

In acetonitrile, byproduct (12) was not obtained, and the yield of compound (13) was increased threefold. However, the more interesting product (14) could not be purified satisfactorily by chromatography on alumina. The compound was not stable to silica, decomposing slowly to give a yellow product. It is possible that the compound underwent desulphurisation to the oxa compound (15). A sample of compound (14), heated with mercuric acetate

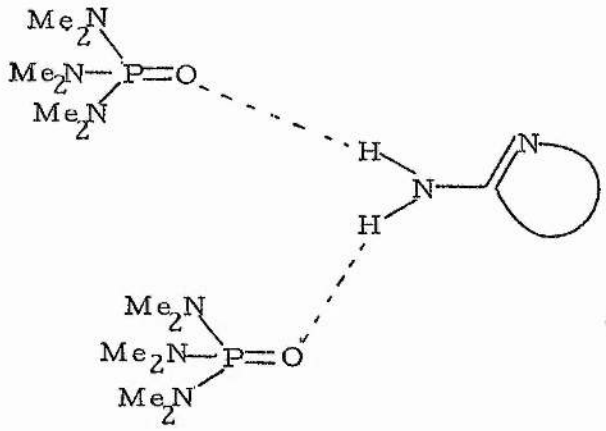


(15)

and acetic acid in a test-tube, gave a yellow product with identical tlc behaviour to the decomposition product, thus apparently confirming that desulphurisation had taken place. The decomposition reaction was not investigated further. Acetonitrile was therefore not a suitable solvent for the reaction.

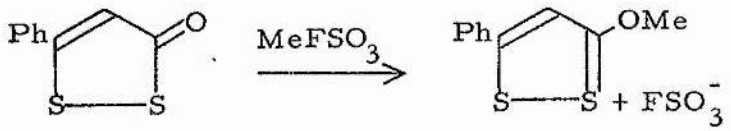
HMPA gave three products. Compound (13) was not formed, and the dithiole-3-one was impure. None of the yields were improved. HMPA may form strong hydrogen bonds (15) with 2-aminoheterocycles, thus inhibiting the reaction of the 2-amino group. This would render HMPA ineffective as a solvent. It was decided to use ethanol as solvent in future reactions.

It was thought that the choice of leaving group might influence the yields of the various products. In order to investigate this possibility, 3-methoxy-5-phenyl-1,2-dithiolium fluorosulphonate



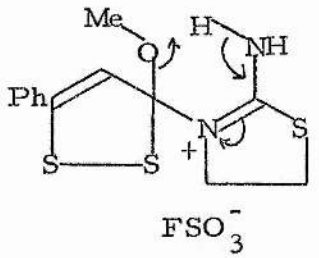
(15)

(16) was synthesised. 5-Phenyl-1,2-dithiole-3-one (12) was boiled with methyl fluorosulphonate in dry benzene and the salt (16) was obtained in good yield.



(12) (16)

The salt (16) reacted with 2-amino-2-thiazoline, giving three products. The yields of the thione (11) and ketone (12) were reduced, and the yellow compound (13) was not obtained at all. However, the yield of the orange compound was increased by a factor of three. One explanation for this increase is that the reaction proceeds via an energetically favourable six-membered transition state (17), when condensation takes place at the heterocyclic nitrogen. It is not surprising that the yields

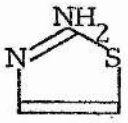


(17)

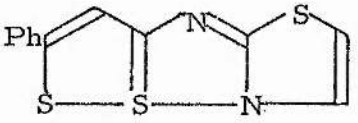
of the other products decreased, as MeO^- is a poorer leaving group than Cl^-.

2. The Reaction of 3-Substituted-5-phenyl-1 ,2-dithiolium Salts with 2-Aminothiazole

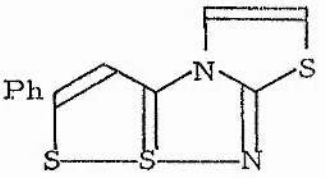
Four products were obtained from the reaction of 2-aminothiazole (18) with 3-chloro-5-phenyl-1, 2-dithiolium chloride. The yields of the triheterapentalenes (19) and (20) were higher than those of the corresponding products from 2-amino-2-thiazoline.



(18)



(19)



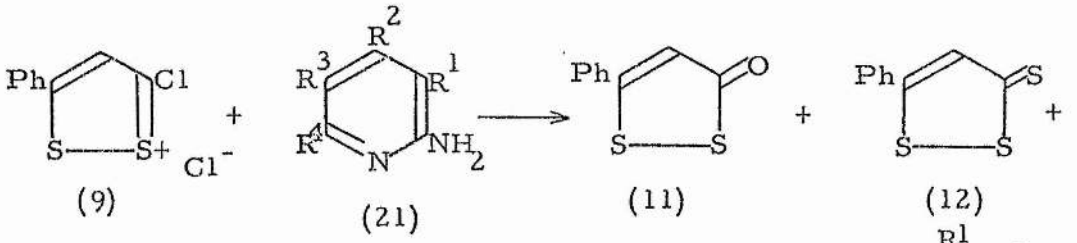
(20)

5-Phenyl-1, 2-dithiole-3-thione (11) and 5-phenyl-1, 2-dithiole-3-one (12) were also formed. Compound (19) and the dithiolone (12) had very similar polarities, which made their separation rather difficult. A pure sample of the dithiolone was not obtained.

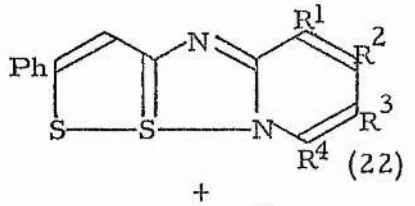
When 3-methoxy-5-phenyl-1,2-dithiolium fluorosulphonate was used in the reaction, the yields of all the products decreased. Compound (20) was not present, and the dithiolone was impure. Formation of compound (20), via a six-membered transition state similar to the one already discussed, would necessitate a disruption of the aromaticity of 2-aminothiazole, and would result in an energetically less favourable pathway than the one taken by 2-amino-2-thiazoline. This would explain the absence of the product (20) in the present reaction.

3. The Reaction of 3-Substituted-5-phenyl-1,2-dithiolium Salts with Various 2-Aminopyridines

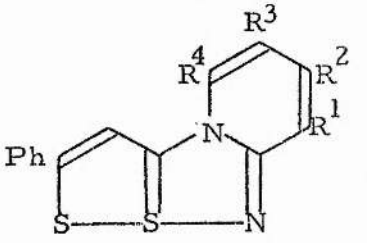
3-Chloro-5-phenyl-1,2-dithiolium chloride (9) reacted with the 2-aminopyridines (21a-f). In every case the byproducts 5-phenyl-1,2-dithiole-3-thione (11) and 5-phenyl-1,2-dithiole-3-one (12) were obtained, in roughly 8% and 40% yield respectively. Each reaction also gave a yellow product. These compounds were formulated as the triheterapentalenes (22a-f). The yields of the yellow products lay between 25% and 40%, except in the case of compound (22b), which was obtained in lower yield (14%). This low yield may have been caused by the partial blocking of the reactive amino group in the starting amine (21b) by the presence of an adjacent methyl group. The separation of compound (22b) from the dithiolone (12) also proved particularly



(9) (21) (11) (12)



(22)



(23)

	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	H	H	H
c	H	Me	H	H
d	H	H	Me	H
e	H	H	H	Me
f	H	Me	H	Me

difficult, and may account in part for the yield being lower than expected.

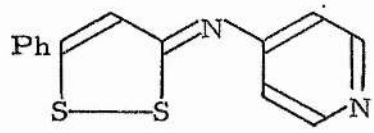
In several cases, a small quantity of a polar red product was obtained. These compounds were formulated as the triheterapentalenes (23a-d). They arise from condensation at the ring nitrogen atom. This assignment was subsequently substantiated when compound (23c) was synthesised by an alternative route (see Part B). In every reaction, the yield of the red product was less than 1%. These compounds were characterised by their mass spectra and by microanalysis. Compounds (23e) and (23f) were not obtained, probably owing to steric blocking of the ring nitrogen in the precursors (21e) and (21f) by neighbouring methyl and amino groups.

When the 3-methoxy salt (16) was allowed to react with 2-amino-4-methylpyridine (21c), the yield of each of the expected products decreased.

Generally, the yield of the less polar product increases by an order of magnitude, and the more polar one decreases, when a 2-aminopyridine replaces a 5-membered aminoheterocycle. Therefore the geometry of the starting material is an important factor in the reaction.

4. The Reaction of 3-Chloro-5-phenyl-1,2-dithiolium Chloride with 4-Aminopyridine

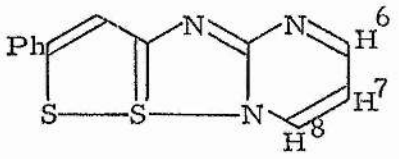
The reaction of 3-chloro-5-phenyl-1,2-dithiolium chloride (9) with 4-aminopyridine produced only a few milligrams of the expected 3-imino-1,2-dithiole (24), accompanied by the byproducts (11) and (12). This low yield is surprising, in view of the fact that 4-aminopyridine is a stronger base than 2-aminopyridine.



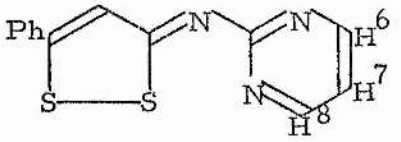
(24)

5. The Reaction of 3-Chloro-5-phenyl-1,2-dithiolium Chloride with 2-Aminopyrimidine

This weaker base reacted with the chlorodithiolium salt (9) to produce a product (25) or (26) in low yield, together with 5-phenyl-1,2-dithiole-3-thione and 5-phenyl-1,2-dithiole-3-one.



(25)



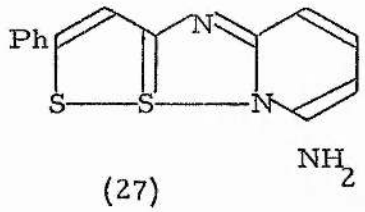
(26)

At room temperature, the ^1H nmr spectrum of this product in chloroform-D_3 was very poorly resolved. The signal of 6-H and 8-H appeared as a broad singlet, and that of 7-H as a poorly resolved triplet, suggesting that 6-H and 8-H were accidentally magnetically equivalent. However, at -24°C, the spectrum had sharpened up considerably, with 6-H and 8-H appearing as a doublet, and 7-H as a triplet. This temperature-dependence indicated that restricted rotation around a double bond was taking place at ambient temperature. At -24°C, the rotation had slowed down. The product therefore appears to possess the 3-imino-1,2-dithiole structure (26). In this structure, 6-H and 8-H would be chemically as well as magnetically equivalent.

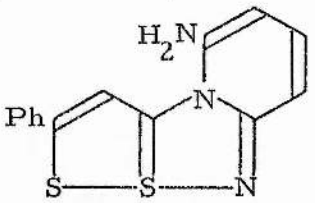
6. The Reaction of 3-Chloro-5-phenyl-1,2-dithiolium Chloride with 2,6-Diaminopyridine

The reaction of 2,6-diaminopyridine with 3-chloro-5-phenyl-1,2-dithiolium chloride (9) gave rise to 5-phenyl-1,2-dithiole-3-thione (11), 5-phenyl-1,2-dithiole-3-one (12), and smaller quantities of two other compounds. These were not

the possible monosubstitution products (27) and (28).

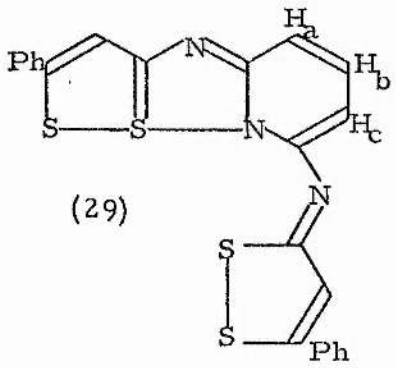


(27)

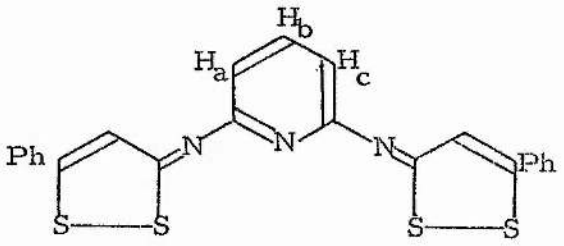


(28)

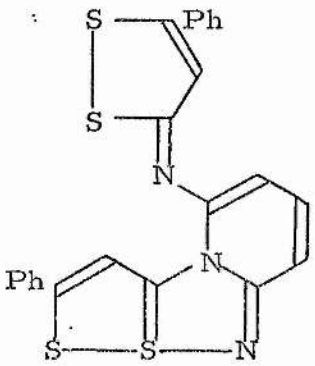
Analytical and mass spectral data showed that the products were the result of the reaction of two molecules of the dithiolium salt (9) with one of 2,6-diaminopyridine. The less polar product was assigned the structure (29) or (30) and the more polar product was designated as compound (31).



(29)



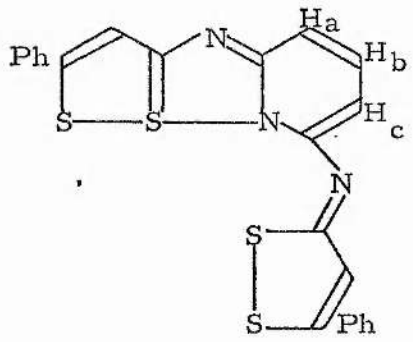
(30)



(31)

^{1}H Nmr spectroscopy should be able to distinguish between structures (29) and (30). In structure (30), H_a and H_c are equivalent and would therefore appear as a doublet, while H_b would be a triplet. The spectrum of structure (29) would show a doublet for H_a, a double doublet for H_b, and a doublet for H_c unless H_a and H_c were accidentally equivalent, in which case the spectrum would be identical to that of structure (30).

Table 2: ^{1}H Nmr Spectrum of Compound (29)



Solvent	Temperature	Chemical Shift ( )	Assignment
$CDCl_3$	Room Temp.	6.30 (d)	H_a or H_c
		6.84 (d)	H_a or H_c
		7.41-7.76 (m)	All other protons
DMSO-D_6	Room Temp.	Absorbtions very weak	
	100°	7.03 (d)	H_a or H_c
		7.18-7.85 (m)	All other protons
		8.30 (d)	H_a or H_c
toluene-D_8	Room Temp.	6.84-7.16 (m)	All protons
	60°	6.84-7.15 (m)	All protons
	80°	6.83-7.24 (m)	All protons
	100°	6.84-7.40 (m)	All protons
pyridine-D_5	Room Temp.	6.91-7.56 (m)	All protons

The ^{1}H nmr spectrum was recorded in chloroform-D_3, dimethyl sulphoxide-D_6, toluene-D_8 and pyridine-D_5. The results are shown in Table 2. Unambiguous assignment of the structure was impossible, owing to the low solubility of the compound and the many overlapping aromatic signals present. In chloroform-D_3 and dimethyl sulphoxide-D_6 two doublets were observed. In no case was it possible to pick out a triplet or a double doublet. Although the presence of two doublets is circumstantial evidence for the structure (29), this evidence cannot be regarded as conclusive unless a double doublet or a triplet can be assigned. The situation could be greatly clarified in future by synthesising a similar compound with alkyl (eg. t-butyl) groups in place of the phenyl groups.

Compound (31) also failed to give a satisfactory ^{1}H nmr spectrum, owing to its insolubility.

Structure (29) is an example of a molecule able to undergo reversible valence isomerisation (see Figure 1).

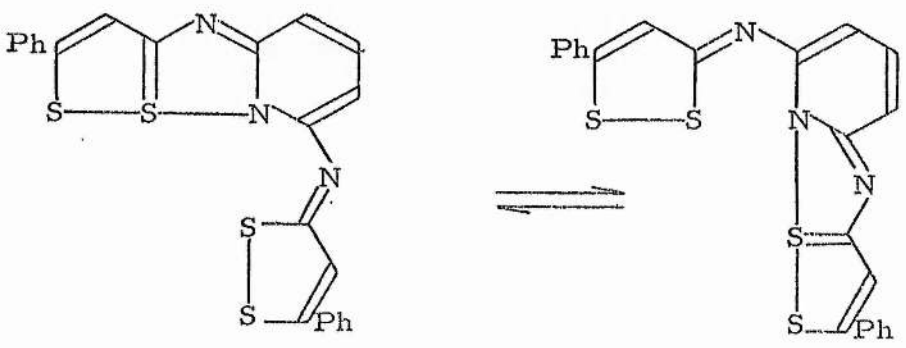


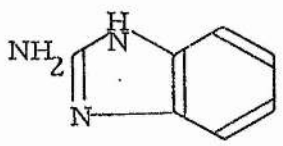
Figure 1: Valence Isomerisation of Structure (29)

Increasing the temperature would speed up the rate of isomerisation. At sufficiently high temperatures this isomerisation would be rapid on the ^{1}H nmr time-scale, and would result in a simpler, time-averaged spectrum being obtained. The ^{1}H nmr spectrum was taken in toluene-D_8 at room temperature, 60°C, 80°C, and 100°C, and in dimethyl sulphoxide-D_6 at room temperature and 100°C. No evidence of time-averaging was observed. In dimethylsulphoxide-D_6 the compound decomposed slowly at high temperature.

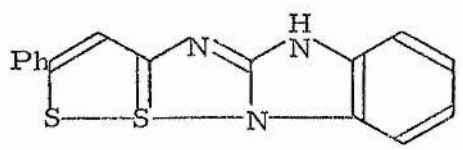
Therefore, either the compound does not possess the structure (29), or a high enough temperature was not attained for the isomerisation to become sufficiently rapid.

7. The Reaction of 3-Chloro-5-phenyl-1,2-dithiolium Chloride with 2-Aminobenzimidazole

The condensation of 2-aminobenzimidazole (32) with 3-chloro-5-phenyl-1,2-dithiolium chloride (9) produced the by now familiar byproducts, namely 5-phenyl-1,2-dithiole-3-thione (11) and 5-phenyl-1,2-dithiole-3-one (12). A yellow product formulated as the dithiatriaza compound (33) was obtained in low yield from this reaction.



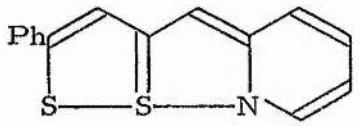
(32)



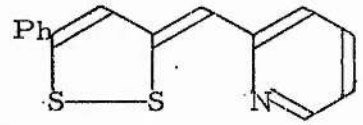
(33)

8. The Reaction of 3-Chloro-5-phenyl-1,2-dithiolium Chloride with 2-Methylpyridine

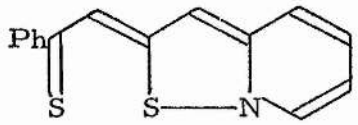
It was decided to investigate the possibility that reaction might take place between the chlorodithiolium salt (9) and 2-methylpyridine. Reaction with the methyl group would result in the formation of a product with structure (34), (35) or (36). Condensation at the heterocyclic nitrogen atom would lead to a product formulated as compound (37), (38) or (39).



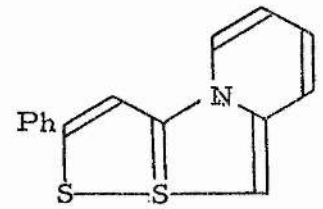
(34)



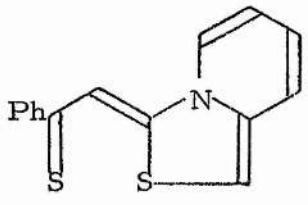
(35)



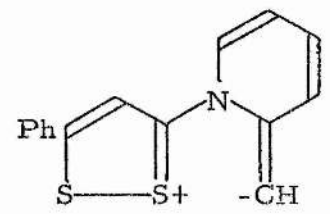
(36)



(37)



(38)

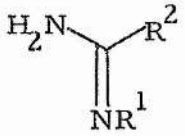


(39)

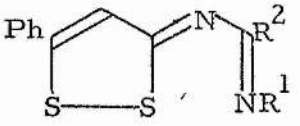
However, in practice, neither of the desired products was obtained.

9. The Reaction of 3-Chloro-5-phenyl-1,2-dithiolium Chloride with N-Phenylbenzamidine

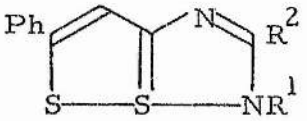
The reactions hitherto investigated have solely concerned heterocyclic amines. Theoretically, amidines with the structure (40) should also react, to give two types of product. Condensation at the amino group would lead to a compound of structure (41), (42)



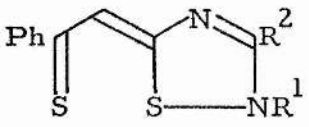
(40)



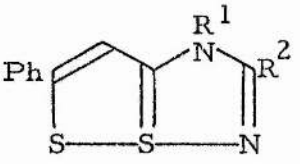
(41)



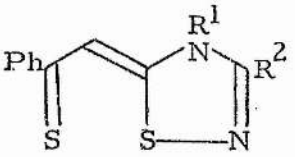
(42)



(43)



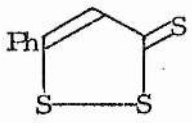
(44)



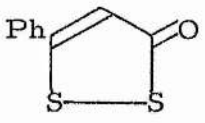
(45)

or (43). Reaction at the imino nitrogen atom would give a compound of structure (44) or (45).

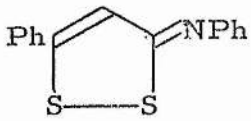
A reaction of this type was carried out, using N-phenylbenzamidine (40, R^1=R^2=Ph) and 3-chloro-5-phenyl-1,2-dithiolium chloride (9). This produced the dithiolone (12), the dithiolethione (11), and a few milligrams of a yellow product tentatively identified as the 3-imino-1,2-dithiole (46), on the basis of its mass spectrum and melting point. [Compound (46) has previously been prepared by the action of aniline on the dithiolium salt (47)[154,155].]



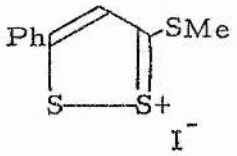
(11)



(12)



(46)

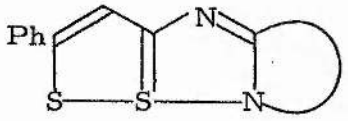


(47)

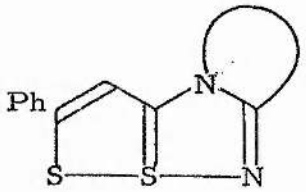
The reaction did not afford either of the expected products. It is suggested that the two phenyl groups of N-phenylbenzamidine blocked the reaction sites. Attempts to synthesise other amidines with less bulky substituents were unsuccessful. The reaction of amidines was not pursued further.

B. SYNTHESIS OF 6-METHYL-2-PHENYL-1, 8aλ^4-DITHIA-3b, 8-DIAZACYCLOPENT[a]INDENE AND ATTEMPTED SYNTHESIS OF 1, 6, 6aλ^4-TRITHIA-3a, 7-DIAZACYCLOPENT[a]PENTALENES

Several of the reactions described in Part A of this discussion gave two isomeric products, formulated in general terms as the structures (4) and (6). In order to distinguish between the two types of structures it was decided to firmly establish the identity of one isomer by an unambiguous synthesis.

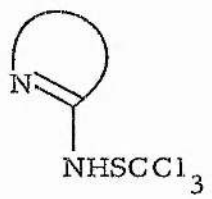


(4)

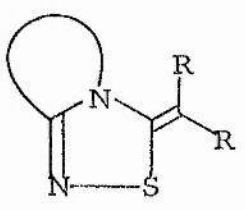


(6)

It would prove valuable to develop an alternative synthesis of compounds having structure (6). These compounds are of greater theoretical interest than the compounds of structure (4). Goerdeler[102], and Potts[101, 103, 104] have developed several syntheses of heterocyclic sulphenamides (48). Potts[101] has discovered that these compounds condense with enolate anions, with accompanying ring-closure, to give compounds of the type (49).

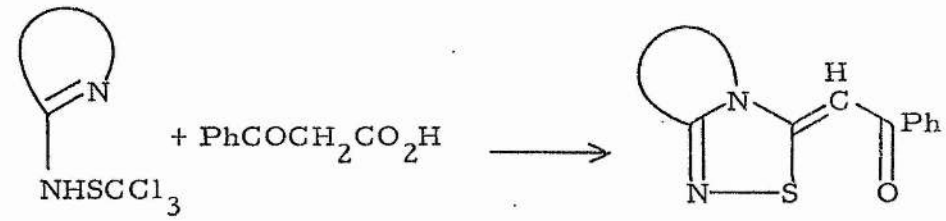


(48)

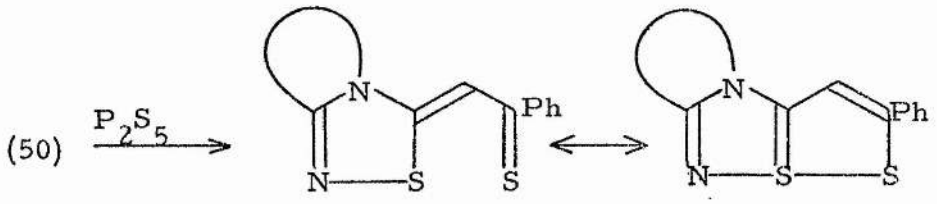


(49)

It was concluded that these reactions could form the basis of a synthesis of compounds of type (6). Condensation of a heterocyclic sulphenamide (48) with benzoylacetic acid, accompanied by decarboxylation, would lead to compound (50). Subsequent thionation would give the product (51), that is, compound (6).



(48) (50)

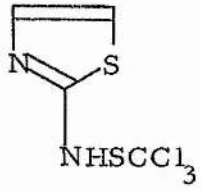


(51) (6)

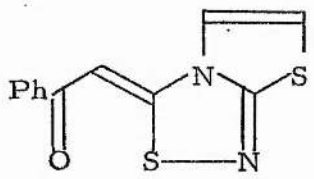
The feasibility of this synthesis was investigated, using 2-aminothiazole, 2-amino-2-thiazoline and 2-amino-4-methylpyridine as starting materials. The appropriate sulphenamides (52)-(54) were readily prepared by modifying the existing syntheses.

The sulphenamide (52) was allowed to condense with benzoylacetic acid in the presence of an excess of triethylamine. Dry dimethylformamide was used as solvent. Acetophenone, produced by the decomposition of benzoylacetic acid, together with a few milligrams of an impure yellow product were obtained.

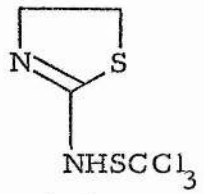
The mass spectrum of this material showed a parent ion at m/e 260. The product was therefore tentatively identified as the oxadithiadiazacyclopent[a]pentalene (55).



(52)



(55)

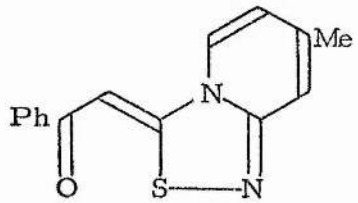


(53)

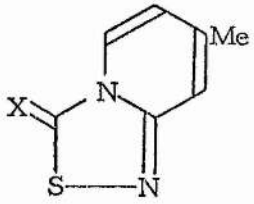
Under similar reaction conditions, the sulphenamide (53) gave no useful products. The reaction was repeated using the sodium salt of benzoylacetic acid, in ethanol, and with an excess of sodium carbonate present. This was also unsuccessful. The reactions of the sulphenamides (52) and (53) were abandoned at this stage. Potts had previously found[103] that certain sulphenamides do not react with enolate anions.

The sulphenamide (54) gave more promising results. The condensation, carried out in dimethylformamide and with an

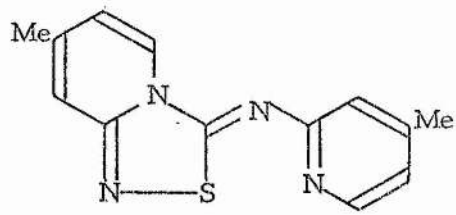
(54)



(56)



(57)

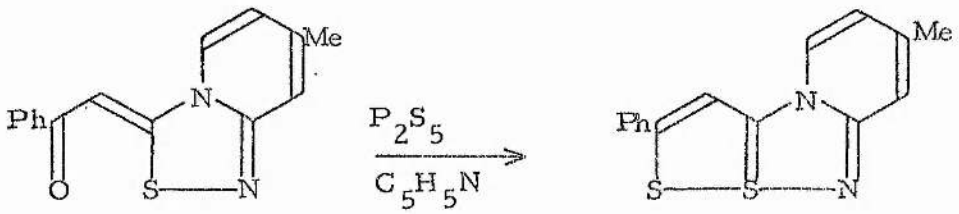


(58)

excess of triethylamine present, gave the desired product (56) in 8% yield. Three byproducts were also obtained from this reaction, principally a colourless product, identified as compound (57, X=O). This product resulted from attack of the sulphenamide by water, accompanied by cyclisation. It is rather surprising that Potts did not observe compounds of this type during his studies. He has, however, prepared compounds similar to (57, X=S), by allowing sulphenamides to react with sodium hydrogen sulphide[101].

The other byproducts were identified by tlc comparison as acetophenone and the [1,2,4]thiadiazolo[4,3-a]pyridine (58). Potts had previously synthesised this compound[100], and has isolated the same compound from the reaction of 2-trichloromethylsulphenamidopyrimidine, with 2-amino-4-methylpyridine[103]. He describes the product as orange needles, m.p. 189-191°. However, a sample of the compound (58) prepared in this laboratory for comparison with the byproduct obtained in the foregoing reaction was obtained as yellow prisms, m.p. 192-194°. This suggests that Potts has failed to purify the compound adequately.

Thionation of compound (56) with phosphorus pentasulphide in dry pyridine gave a thionation product in poor yield. This



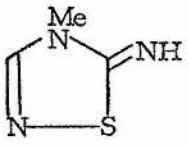
(56) (23c)

product was identical (m.p., mixed m.p., mass spectrum) with the more polar product obtained from the reaction of 2-amino-4-methylpyridine with 3-chloro-5-phenyl-1,2-dithiolium chloride (see page 53), and is therefore the dithiadiazacyclopent[a]indene (23c). An appreciable quantity of starting material (56) was also recovered, accompanied by a trace of 5-phenyl-1,2-dithiole-3-thione.

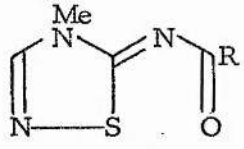
Thus it is confirmed that the more polar product obtained from the reaction of 3-chloro-5-phenyl-1,2-dithiolium chloride with 2-amino-4-methylpyridine results from condensation at the ring nitrogen atom of the amine. It is possible to extrapolate to include the other 2-aminoheterocycles which gave two products on reaction with the 1,2-dithiolium salts. In every case a yellow, less polar product and a more deeply coloured and more polar product were obtained. It is therefore concluded, with some degree of confidence, that the more polar of the two compounds formed in these reactions results from condensation at the ring nitrogen atom, and may be formulated as a triheterapentalene containing a pyridine-type nitrogen atom in the three-centre bonded sequence.

C. SYNTHESIS OF 1H- and 6H-TRIHETERAPENTALENES

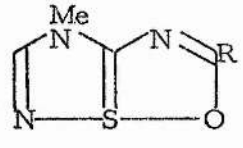
The introductory section of this thesis contains a description of several classes of compound based on the 1,2,4-thiadiazole system, which may be reformulated as triheterapentalenes. Many of the compounds discussed were prepared by Goerdeler and coworkers, who used the imino-1,2,4-thiadiazole (59) as a starting material in syntheses of compounds with the general formula (60).



(59)



(60)



(61)

The products (60) can also be formulated as bicyclic compounds (61), which are triheterapentalenes containing a pyridine-type nitrogen atom in the three-centre bonded sequence, and are therefore of relevance to the work embodied in this thesis.

However, although triheterapentalenes containing the N-S-O sequence have previously been synthesised[156], their structure has not been indisputably ascertained. X-Ray crystallographic studies of oxathiapentalenes (see introduction, section A) have shown that the S-O interactions observed in these compounds are rather weak.

In view of the uncertainty about the nature of the bonding in oxathiaazapentalenes, the compounds prepared by Goerdeler are

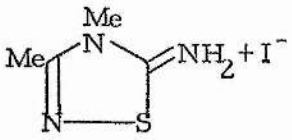
of rather limited interest. It should prove more valuable to synthesise similar compounds where sulphur or nitrogen replaces the oxygen atom, as S-S and S-N bonds in triheteropentalenes are generally stronger than S-O bonds. Attempts to prepare such compounds, both by new methods and by extensions of established procedures, are described below. The compounds synthesised may be formulated as monocyclic or bicyclic structures. Bicyclic formulations are used throughout.

Goerdeler has utilised the imine (59) as a substrate in several reactions. Although this type of compound makes a convenient starting material, the use of this particular compound is disadvantageous. 4,5-Dihydro-5-imino-1,2,4-thiadiazoles, (62), which are unsubstituted in the 3-position, have been shown to rearrange[113], in high yield, and under fairly mild conditions, to compounds (63). The presence of these potentially reactive substrates in a reaction is undesirable. It was therefore decided to use iminothiadiazoles which were substituted at position 3, as

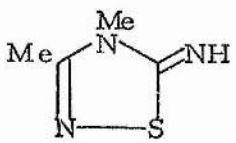
(62) (63)

these compounds are much less susceptible to rearrangement[113].

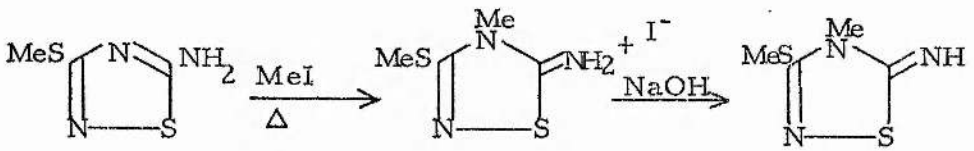
The salt (65a) and the imino-compound (66a) were readily prepared using the established methods. The salt (65b) was obtained in good yield by boiling 5-amino-3-methylthio-1,2,4-thiadiazole (64) with methyl iodide. Neutralisation with dilute sodium hydroxide solution gave the imine (66b) quantitatively.



(65a)



(66a)



(64) (65b) (66b)

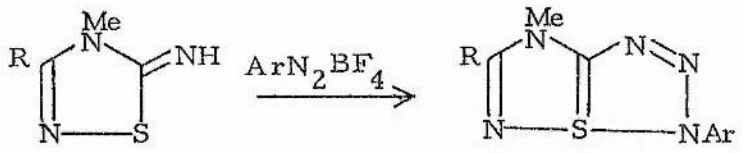
Methyl- and methylthio-substituted starting materials were chosen because the simplicity of their structure simplifies ^{1}H nmr spectral studies, and because they are readily available.

1. Synthesis of Thiaazapentalenes

a. Synthesis of 3,5,6-Trisubstituted-6H-3aλ^{4}-thia-1,2,3,4,6-pentaazapentalenes

The imino compounds (66a) and (66b) coupled with arenediazonium fluoroborates in acetonitrile containing 5% pyridine at room temperature. The expected products,

formulated as the bicyclic species (67a-d), were obtained in yields ranging from 8% to 50%.



(66) (67a-d)

	R	Ar
a	Me	Ph
b	Me	$pNO_2C_6H_4$
c	MeS	Ph
d	MeS	$pNO_2C_6H_4$

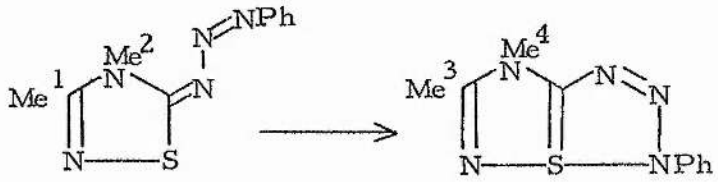
Two yellow products were formed in the synthesis of compound (67b). This mixture was converted into a single compound by dissolving it in chloroform and boiling the solution in the presence of alumina. The resulting product had identical tlc behaviour to the slower-running component of the original mixture. A pure solid sample of the slower-running product, which had been left standing in daylight for a few days, showed two spots on tlc . This indicated that isomerisation was taking place.

Further evidence of this was obtained using ^1H nmr spectroscopy. The spectrum of the mixture in chloroform-D_3 contained aromatic proton resonances, and two pairs of signals corresponding to four methyl groups in the approximate ratio of 3:1. As time elapsed, the ratio of the pairs of signals altered, until, after 24 hours, the spectrum was identical to that of the more polar component of the mixture (see Table 3).

Photochemical isomerisation of solutions of trithiapentalenes[157], oxadithiapentalenes[158-161] and dithiaazapentalenes[162] have previously been studied by other workers. Irradiation with

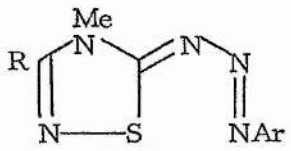
ultraviolet light results in the formation of a photoproduct, which quickly reverts to the starting material in a dark reaction.

Table 3: Isomerisation of Compound (67b) - Variation of ^{1}H nmr Spectrum with Time

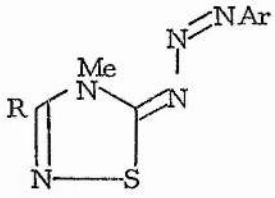


Time (hours)	Me^1	Me^2	Me^3	Me^4	Ratio Me^3:Me^1
0	δ 2.43	δ 3.32	δ 2.56	δ 3.86	3:10
$1\frac{1}{2}$	2.43	3.32	2.56	3.86	2:3
4	2.43	3.32	2.56	3.86	1:1
$6\frac{3}{4}$	2.43	3.32	2.56	3.86	3:2
24	-	-	2.59	3.86	∞

The photoproduct is generally accepted as being a trans-isomer of the starting material. However, the isomerisation encountered in the present case is persistent. The fact that daylight can induce isomerisation suggests that any three-centre bonding present in the product is a weak interaction, which requires only relatively low-energy radiation to disrupt it. The products may therefore best be represented as the cis- and trans- structures (68) and (69).



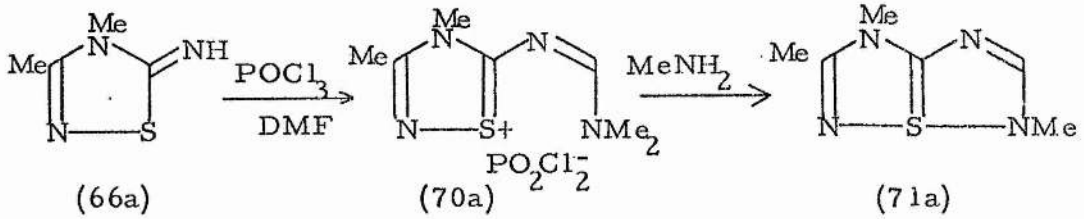
(68)



(69)

b. Synthesis of 1,2,4-Trisubstituted-1H-3aλ^4-thia-1,3,4,6-tetraazapentalenes

The imine (66a) reacted with a previously prepared solution of phosphoryl chloride in dimethylformamide, at room temperature, to form a solution of the Vilsmeier salt (70a). This salt, which was not isolated, reacted with aqueous methylamine, yielding a

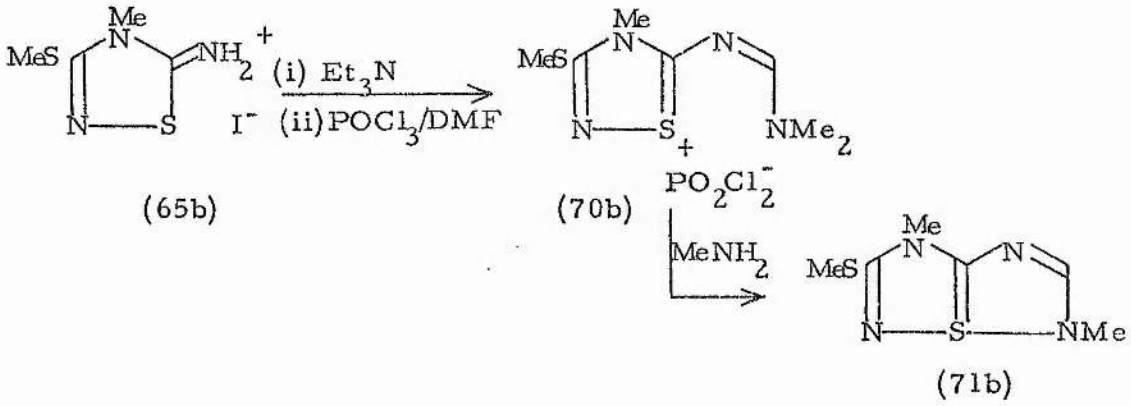


(66a) (70a) (71a)

colourless product formulated as the thiatetraazapentalene (71a, R=Me), in 23% yield.

Compound (71b) was prepared directly from the thiadiazolium salt (65b). A solution of the salt in dimethylformamide was treated with triethylamine, followed by phosphoryl chloride, to give the Vilsmeier salt (70b) in solution. Condensation with aqueous

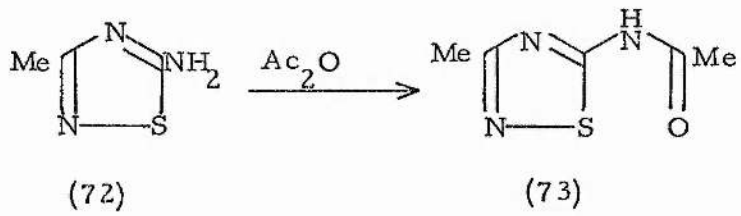
methylamine gave the desired product (71b) in 56% yield.



2. Synthesis of Oxa- and Selena-thiaazapentalenes

a. Preparation of 5-Acetamino-3-methyl-1,2,4-thiadiazole

The 1,2,4-thiadiazole (72), when boiled in acetic anhydride for 30 minutes, gave 5-acetamino-3-methyl-1,2,4-thiadiazole (73) in 94% yield.

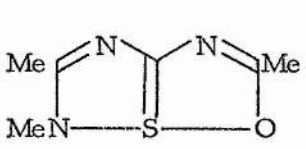


b. Synthesis of 2,5,6-Trimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalene

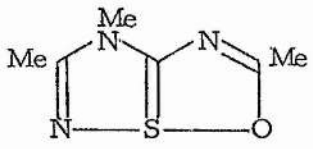
(i) Methylation of 5-Acetamino-3-methyl-1,2,4-thiadiazole

5-Acetamino-3-methyl-1,2,4-thiadiazole (73) is potentially a precursor of 1,6,6aλ^4-triheterapentalenes, as well as the

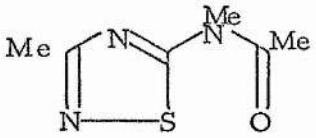
6H-triheterapentalenes which are the principal concern of the present work. There are three possible sites for N-methylation in compound (73). Methylation followed by neutralisation of the resulting salt could therefore give three different isomeric products, (74), (75) and (76).



(74)



(75)



(76)

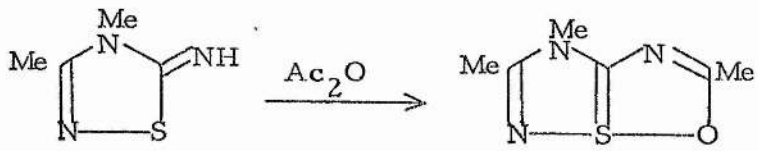
Compound (74) would arise from methylation at N-2, and is an example of the conventional type of 1,6,6aλ^4-triheterapentalene. Methylation at N-4 would lead to compound (75), a 6H-triheterapentalene. Reaction with the nitrogen atom in the side-chain would give the 1,2,4-thiadiazole derivative (76).

Methylation of compound (73), in boiling dry benzene, was carried out with methyl fluorosulphonate. Neutralisation of the glassy product with sodium carbonate gave compound (75) in 35% yield. The structure of this product was confirmed by an unequivocal synthesis, which will now be described.

(ii) Acetylation of 4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole

The imine (66a) was stirred in acetic anhydride for 30 minutes at room temperature. The colourless oxathiatriazapentalene (75) was formed in 47% yield. This compound was identical (melting

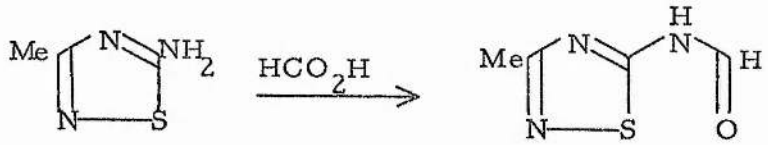
point, mixed melting point, mass spectrum, ^{1}H nmr spectrum) to the sample prepared by the immediately preceding method (i).



(66a) (75)

c. Preparation of 5-Formamino-3-methyl-1,2,4-thiadiazole

The thiadiazole (72) was boiled with formic acid in xylene for 24 hours, affording a mixture of 5-formamino-3-methyl-1,2,4-thiadiazole (77) and unreacted starting material. ^{1}H Nmr spectroscopy showed that the product:substrate ratio was approximately 7:1. Two successive crystallisations of the mixture



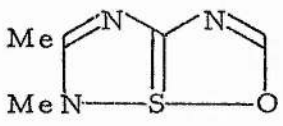
(72) (77)

from ethanol gave the desired product (77) as colourless prisms, in 52% yield.

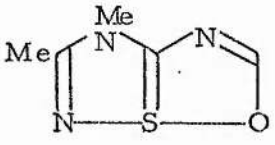
d. Synthesis and Attempted Synthesis of 5,6-Disubstituted-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalenes

(i) Methylation of 5-Formamino-3-methyl-1,2,4-thiadiazole

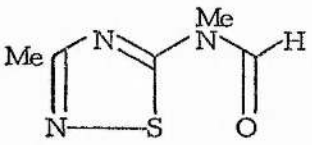
The thiadiazole (77) is similar to 5-acetamino-3-methyl-1,2,4-thiadiazole in that it has three possible sites for N-methylation. Methylation at N-2 would lead to the triheterapentalene (78), reaction at N-4 to the 6H-triheterapentalene (79a) while methylation in the side-chain would give the thiadiazole (80).



(78)



(79a)



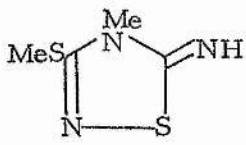
(80)

Methylation was carried out using methyl fluorosulphonate in dry chloroform. Treatment of the tarry product with an excess of aqueous sodium carbonate gave compound (79a) in low yield. It was confirmed that the correct structure had been assigned to compound (79a), when the same compound was synthesised by an alternative route (see (iii) below).

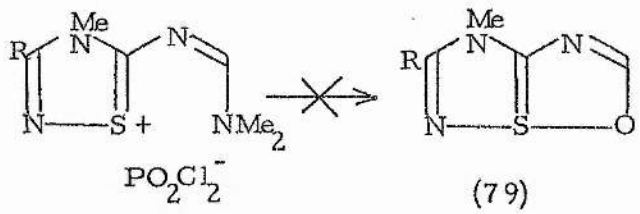
(ii) Attempted Formylation of the Vilsmeier Salts (70)

Solutions of the Vilsmeier salts (70a) and (70b) were treated with dilute sodium hydroxide. The expected products (79a) and (79b) were not formed. No useful material was obtained from

the salt (70a). However, the salt (70b) afforded the imine (66b)



(66b)



(70) (79)

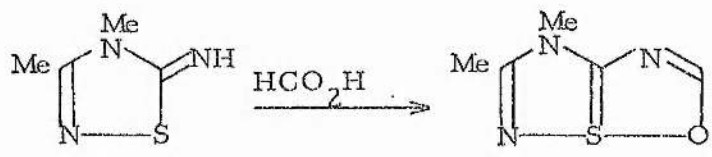
a, R=Me; b, R=SMe

in 50% yield.

It is somewhat surprising that the reaction failed to give the desired products, which are stable compounds, and which were successfully synthesised by other routes. The reactivity of the Vilsmeier salts (70a) and (70b) is not open to question, as they have already been shown to react successfully with methylamine. Also, in section 3 of this discussion, the successful reaction of the Vilsmeier salts (70a) and (70b) with sodium hydrogen sulphide will be described.

(iii) Formylation of 4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole

The imine (66a) was stirred in formic acid for 30 minutes and gave the oxathiatriazapentalene (79a) in 56% yield. This compound was identical (mass spectrum, ^{1}H nmr spectrum,

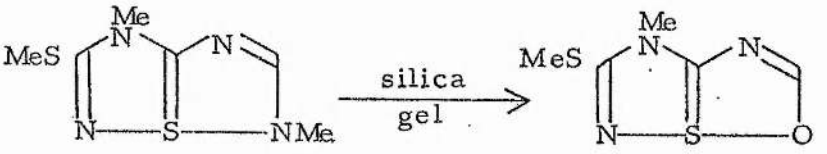


(66a) (79a)

melting point) to the sample previously prepared from 5-formamino-3-methyl-1,2,4-thiadiazole.

(iv) Hydrolysis of 1,4-Dimethyl-2-methylthio-1H-3aλ^4-thia-1,3,4,6-tetraazapentalene

The triheterapentalene (71b) was adsorbed on to a column of silica, and the column was eluted with ether. This afforded the triheterapentalene (79b) in 35% yield. The ease of hydrolysis of

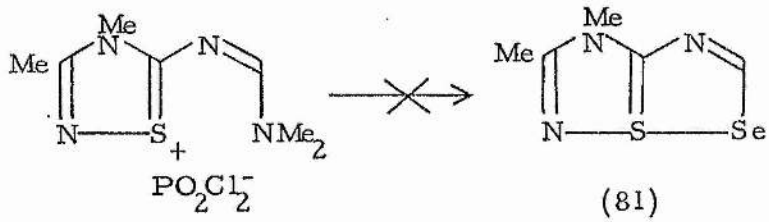


(71b) (79b)

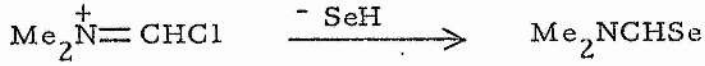
compound (71b) gives an indication of the lability of compounds containing the N-S-N sequence.

e. Attempted Synthesis of 5,6-Dimethyl-6H-3aλ^4-thia-3-selena-1,4,6-triazapentalene

A solution of the Vilsmeier salt (70a) was treated with sodium hydrogen selenide. Instead of the expected product (81), a quantity of dimethylselenoformamide (83) was obtained. This compound was identified by its ^{1}H nmr spectrum, mass spectrum and boiling point. The product (83) presumably arose from reaction of the Vilsmeier reagent (82) with sodium hydrogen selenide.



(70a) (81)



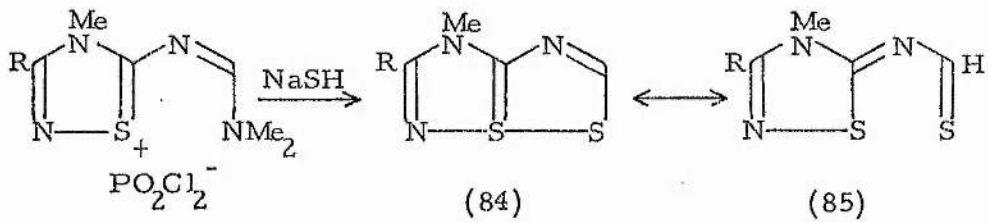
(82) (83)

3. Synthesis of Dithiaazapentalenes

a. Synthesis of 5,6-Disubstituted-6H-3,3aλ^4-dithia-1,4,6-triazapentalenes

(i) Thioformylation of the Vilsmeier Salts (70)

Solutions of the Vilsmeier salts (70a) and (70b) were treated with sodium hydrogen sulphide solution, and gave the dithiatriazapentalenes (84a) and (84b), in 35 and 58% yield respectively.



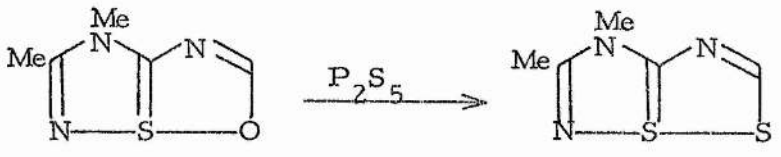
(70) (84) (85)

a, R=Me; b, R=MeS

The ^{1}H nmr spectrum of each product contains an absorption at ca δ 10.5, corresponding to the ring proton. It is known[37] that a proton lying adjacent to a sulphur atom, in a 1,6,6aλ^4-trithiapentalene generally resonates at between δ 8.5 and 9.4, whereas the aldehydic proton of a heterocyclic thioaldehyde generally resonates downfield of δ 10.2[46,47]. This suggests that the products (84a) and (84b) have the thioaldehyde-type structure (85). This evidence cannot be regarded as being conclusive, as it may be argued that the presence of two electron-withdrawing groups adjacent to the ring proton could cause a large deshielding effect, similar to the deshielding observed in this case.

(ii) Thionation of 5,6-Dimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triaza-pentalene

The triheterapentalene (79a) was boiled with phosphorus pentasulphide in dry pyridine, and gave the product (84a) in good yield. This product was identical (m.p., mixed m.p., mass spectrum, ^{1}H nmr spectrum) with the sample prepared by the Vilsmeier reaction.

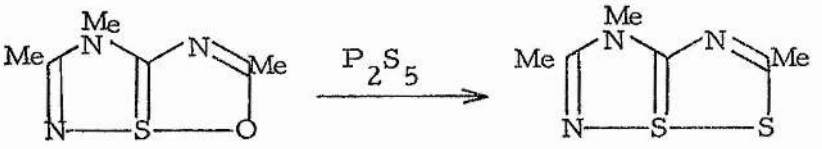


(79a) (84a)

b. Synthesis of 2,5,6-Trisubstituted-6H-3,3aλ^4-dithia-1,4,6-triazapentalenes

(i) Thionation of 2,5,6-Trimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalene

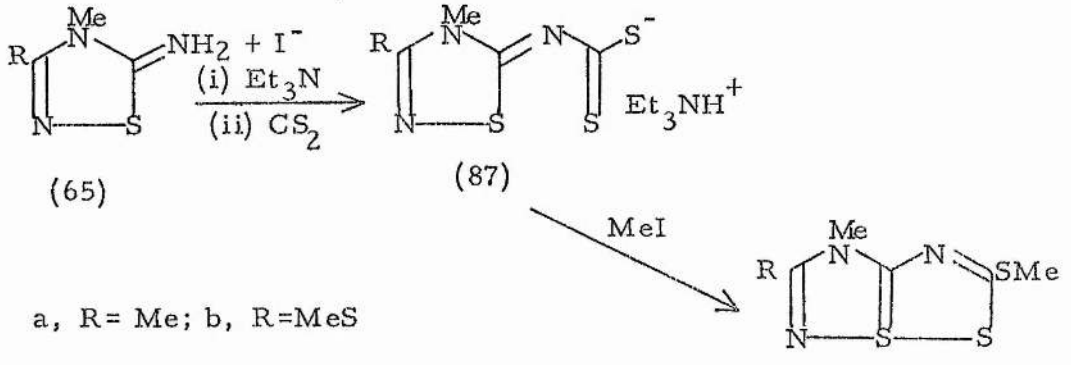
The triheterapentalene (75) was boiled with phosphorus pentasulphide in toluene to give the yellow product (86) in 40% yield.



(75) (86)

(ii) The Reaction of Carbon Disulphide with the Salts (65)

Solutions of the salts (65a) and (65b) were treated with an excess of triethylamine, followed by carbon disulphide. The resulting red solutions, which were believed to contain the intermediates (87a) and (87b), were treated with an excess of methyl iodide, and rapidly decolourised to give the pale yellow products (88a) and (88b) in moderate yield.



(65) (87) (88)

a, R= Me; b, R=MeS

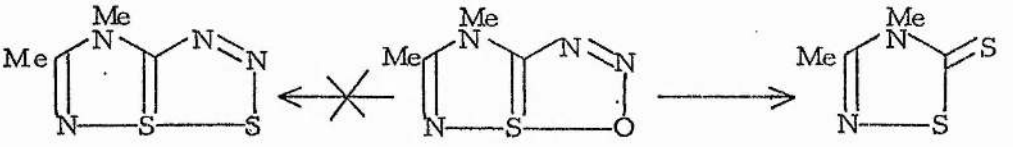
4. Attempted Synthesis of 5,6-Dimethyl-6H-3,3aλ^4-dithia-1,2,4,6-tetraazapentalene

a. Preparation of 5,6-Dimethyl-6H-3-oxa-3aλ^4-thia-1,2,4,6-tetraazapentalene

The triheterapentalene (89) was obtained in moderate yield from the thiadiazolium salt (65a) using a slight modification of the established procedure for the nitrosation of 5-imino-1,2,4-thiadiazoles[107].

b. Attempted Thionation of 5,6-Dimethyl-6H-3-oxa-3aλ^4-thia-1,2,4,6-tetraazapentalene

When compound (89) was boiled with phosphorus pentasulphide in pyridine, the expected thionation product (90) was not formed. Instead, the colourless thione (91) was obtained in modest yield.

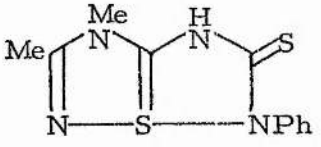


(90) (89) (91)

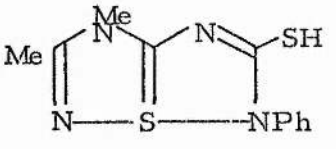
This product arises from the decomposition of the substrate (89) by thionation and loss of the elements of N_2O. When the reaction was repeated using toluene as solvent, brown oxides of nitrogen were seen to be liberated.

5. The Reaction of 4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole with Iso(thio)cyanate

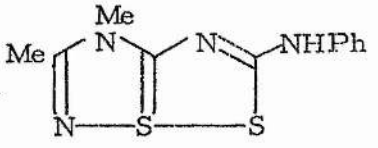
The imine (66a) reacted with phenyl isothiocyanate giving rise to a colourless product in high yield. This product could be represented by one of several different isomeric formulae. Compound (92) is a rare example of a triheterapentalene containing an exocyclic double bond. Rearrangement of compound (92) would



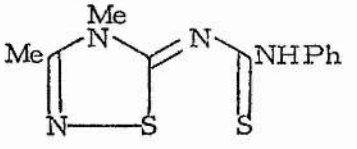
(92)



(93)



(94)

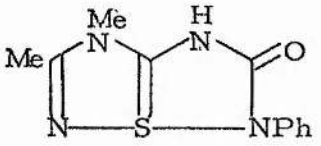


(95)

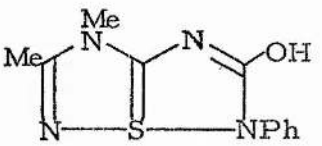
give rise to the fully aromatic triheterapentalene (93). Compound (94) would be formed by reaction with phenyl isothiocyanate, followed by a prototropic shift. This compound may be reformulated as the monocyclic structure (95). The ^{1}H nmr spectrum of the product has a very broad absorbtion at δ 8.44, corresponding to one proton. This is likely to be a >NH absorbtion, as thiols generally resonate at much higher field. Therefore structure (93) can be ruled out. No further definite assignment of the structure

could be made, although it is possible to argue that structures (94) and (95) can be discarded on grounds of colour. The reaction product is colourless, whereas all the other compounds synthesised during the course of this work, which contained the S-S-N sequence, were yellow in colour.

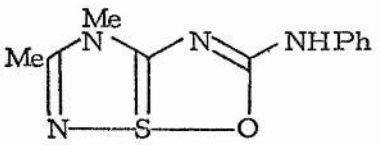
The reaction of phenyl isocyanate with the imine (66a) led to the formation of a colourless product in good yield. The compound has four possible structures, (96)-(99).



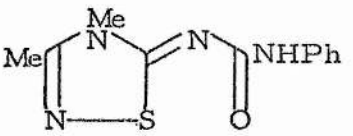
(96)



(97)



(98)



(99)

Positive assignment of the correct structure is more difficult in this case. Structure (97) cannot be disregarded as -OH absorbtions can be found almost anywhere in the ^{1}H nmr spectrum.

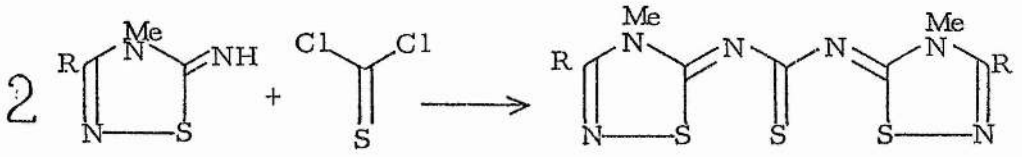
Conclusion

The foregoing results show that it is possible to synthesise compounds which may be formulated as triheteropentalenes containing the novel feature of a pyridine-type nitrogen atom in the three-centre bonded sequence. These compounds have been prepared both by new methods and by extending previous syntheses.

It has not been possible to firmly establish the exact structural nature of these compounds, although several pieces of evidence, such as the isomerisation of the pentaaza compound (67b) and the chemical shift of the ring proton in compounds (84a) and (84b) would seem to indicate that the structures are monocyclic. X-Ray crystal structure determinations of several of the compounds described here are currently being carried out in this department.

6. The Reaction of Thiophosgene with 4,5-Dihydro-5-imino-1,2,4-thiadiazoles

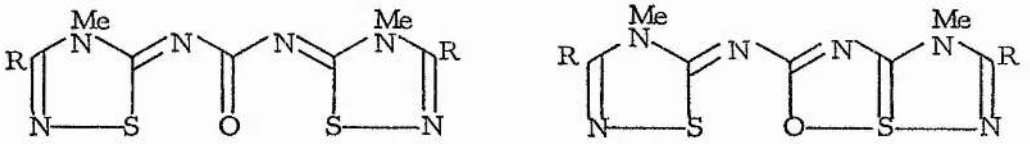
It was decided to investigate the possibility that the imines (66a) and (66b) would react with thiophosgene (100) to give the products (101a) and (101b), which have the potential to exhibit five-centre bonding. Five-centre bonded systems which consist of an array of three sulphur and two nitrogen atoms have not hitherto been synthesised.



(66) (100) (101)

a, R=Me; b, R=MeS

An excess of the imine (66a) or (66b), dissolved in sodium dry benzene, was allowed to react with thiophosgene, in the presence of an excess of triethylamine. The products were found to be oxygen-containing compounds, formulated as (102a) and (102b) or (103a) and (103b).



(102) (103)

a, R=Me; b, R=MeS

The ^{1}H nmr spectra of the products contained only two broad signals, thus implying that both the methyl groups and both the R-groups were equivalent. It is not possible to say whether this equivalence is real, as in (102a) and (102b), or merely a time-dependent effect, caused by the rapid interconversion of two equivalent valence isomers of compound (103) (see Figure 2). Low-temperature ^{1}H nmr studies of the products were not feasible,

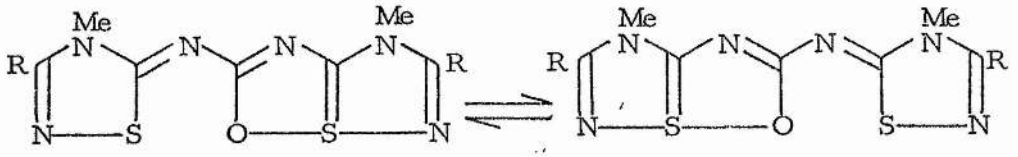


Figure 2: Valence Isomerisation of Compound (103)

owing to their low solubilities.

It was concluded that the sulphur-containing products (101) had been formed but were unstable, undergoing hydrolysis to the oxygen analogues (102).

7. The Use of 6H-Triheterapentalenes as Oil Additives

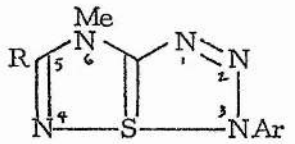
One of the aims of this project was to prepare new triheterapentalenes for assessment as potential lubricating oil additives. Unfortunately, the 6H-triheterapentalenes prepared during the course of this work proved to be rather insoluble in mineral oils, and hence their performance could not be evaluated.

The question of low oil-solubility of certain triheterapentalenes had been encountered in a previous case[90]. This problem was alleviated by the addition of long-chain alkyl groups to the compounds, which increased their solubilities sufficiently to enable them to undergo bench-testing. It is hoped that similar modifications will be carried out to the 6H-triheterapentalenes

synthesised during the course of the current work.

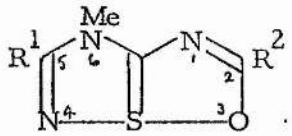
A few of the compounds synthesised proved soluble enough to be tested as potential inhibitors of corrosion in copper. The compounds were dissolved in oil, and then heated for several hours in the presence of a copper strip. The amount of tarnishing and pitting in each strip was compared with a blank sample, a sample containing a corrosion inhibitor known to be effective, and with standard examples of tarnishing and pitting. The results showed that the 6H-triheterapentalenes had no advantage over known commercial corrosion inhibitors.

Table 4: ^{1}H Nmr Spectra of 6H-3aλ^4-Thia-1,2,3,4,6-pentaazapentalenes



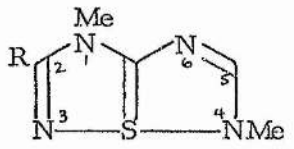
Compound	3-Ar	5-R	6-Me
76a	7.30-7.52 (3H, m, m- and p-H) 7.68-7.81 (2H, m, o-H)	2.46	3.75
76b	7.78, 7.87 (2H, o-H) 8.25, 8.34 (2H, m-H)	2.57	3.87
76c	7.25-7.78 (5H, m, aromatic H)	2.64	3.29
76d	7.71, 7.80 (2H, o-H) 8.17, 8.26 (2H, m-H)	2.64	3.72

Table 5: ^{1}H Nmr Spectra of 6H-3-Oxa-3aλ^4-thia-1,4,6-triaza-pentalenes



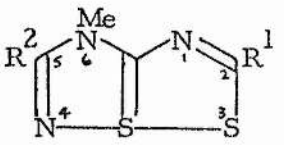
Compound	2-R^2	5-R^1	6-Me
75	2.36	2.50	3.70
79a	9.0 (br)	2.53	3.73
79b	9.0 (br)	2.70	3.67

Table 6: ^{1}H Nmr Spectra of 1H-3aλ^4-Thia-1,3,4,6-tetraaza-pentalenes



Compound	1-Me	2-R	4-Me	5-H
71a	3.61	2.43	3.38 (d, J_{4Me-5H} 1.3)	8.25(q, poorly r)
71b	3.55	2.62	3.36 (d, J_{4Me-5H} 1.4)	8.20(q, poorly r)

Table 7: ^{1}H Nmr Spectra of 6H-3,3aλ^4-Dithia-1,4,6-triazapentalenes



Compound	2-R^1	5-R^2	6-Me
84a	10.51	2.59	3.96
84b	10.46	2.71	3.79
86	2.56	2.84	3.83
88a	2.62*	2.53*	3.75
88b	2.70*	2.76*	3.78

* Tentative assignment

EXPERIMENTAL

Introductory Notes

Melting points were determined on a Kofler hot-stage apparatus and are corrected. Yields refer to recrystallised tlc pure material, unless otherwise stated.

Ultraviolet and visible spectra were measured using a Unicam SP800 spectrophotometer. Light absorbtion data refer to solutions in cyclohexane unless stated otherwise. Infrared spectra were recorded with a Perkin-Elmer 621 spectrometer, and refer to solids dispersed in KBr discs. Mass spectra and accurate mass determinations were carried out on an AEI MS902 instrument.

^{1}H Nmr spectra were recorded at ca 31.4°C, unless otherwise stated, using a Varian HA100 spectrometer operating at 100 MHz. Solutions in chloroform-D_3, toluene-D_8 and pyridine-D_5 were 0.4 M, those in dimethyl sulphoxide-D_6 and trifluoroacetic acid were 0.6 M. When these concentrations could not be attained, saturated solutions were employed. Chemical shifts (δ) are given in ppm downfield from tetramethylsilane as internal reference, except in variable temperature studies, where hexamethyldisiloxane was used. J Values were measured on the 100 Hz scale. Unless otherwise stated (d=doublet, t=triplet, q=quartet, dd=double doublet, dt=double triplet, ddd=double double doublet, m=multiplet and b=broad peak), chemical shift values refer to singlet absorbtions.

Carbon, hydrogen and nitrogen elementary microanalyses were executed by Mr. J. Bews and Mrs. S. Smith, Department of Chemistry, University of St. Andrews. Sulphur elemental analyses

were carried out by Dr. Strauss, Dyson Perrins Laboratory, South Parks Road, Oxford and Dr. A.Bernhardt, Mulheim, West Germany.

Procedures. Criteria used in the identification of products included melting points, tlc behaviour and nmr and mass spectra.

Thin layer chromatography (tlc) was carried out with silica (MN Kieselgel-G) and alumina (MN Aluminium Oxide-G) coated plates (ca 0.25 mM thick). Column chromatography was performed using Merck Activity II-III (70-230 mesh) alumina unless otherwise stated. Chromatographic silica was Sorbsil Silica Gel M60. Solvent mixtures are described in ratios by volume.

Solutions were dried over anhydrous sodium sulphate and solvents were evaporated at reduced pressure with a rotary film evaporator. Solids were dried in vacuo over phosphoric anhydride.

Materials. "Petroleum" refers to petroleum ether of boiling range 40-60° and "ether" refers to diethyl ether. Acetic acid, acetone, cyclohexane, ethanol, methanol, n-hexane, petroleum and pyridine were all redistilled commercial solvents. Ether, benzene, toluene and xylene were refluxed over sodium wire for one hour and then distilled to give the dry solvents. These solvents were stored over sodium wire. The crude ether was pre-dried over calcium chloride for ca. 3 days before refluxing and distilling.

Benzene for chromatography was dried by azeotropic distillation, the first 25% of the distillate being used for extractions. Ether for chromatography was dried over calcium chloride and then distilled.

Methylene chloride was refluxed over phosphoric anhydride for one hour and then distilled.

Acetonitrile was refluxed over sodium hydride (50% dispersion in oil, 2 g per litre) for 30 minutes, distilled, then refluxed over phosphoric anhydride for one hour and redistilled twice.

Dimethylformamide was dried for ca. one week over powdered calcium hydride and then distilled at 15 mm Hg.

Acetic anhydride, ethyl cinnamate, formic acid, perchloromethyl mercaptan, phenyl isocyanate, phenylisothiocyanate, phosphoryl chloride, and thiophosgene were all distilled commercial reagents. Methyl fluorosulphonate was a distilled commercial reagent, and was stored under refrigeration in a polythene bottle. Carbon disulphide was analar grade.

Heterocyclic amines used were commercial reagents. The solids were purified by recrystallisation from benzene, or ethanol, while the liquids were redistilled.

Aqueous methylamine was 25-30% (w/v) methylamine.

Aqueous 4M-sodium hydrogen sulphide solutions were prepared by saturating aqueous 4M-sodium sulphide solutions with hydrogen sulphide. Sodium hydrogen selenide was prepared by the method of Klayman[164].

A. THE REACTION OF 3-SUBSTITUTED-5-PHENYL-1,2-DITHIOLIUM SALTS WITH HETEROCYCLIC AMINES

Preparation of 1,2-Dithiolium Salts

3-Chloro-5-phenyl-1,2-dithiolium Chloride (9)

5-Phenyl-1,2-dithiole-3-one was prepared by Klingsberg's method[165], and converted to 3-chloro-5-phenyl-1,2-dithiolium chloride according to the procedure described by Faust and Mayer[166].

3-Methoxy-5-phenyl-1,2-dithiolium Fluorosulphonate (16)

5-Phenyl-1,2-dithiole-3-one (50 mM, 9.715 g) was dissolved, with warming, in sodium dry benzene (25 ml). Methyl fluorosulphonate (150 mM, 12.1 ml, 17.11 g) was added to the solution, which was then refluxed on an oil bath. Several minutes later a white solid began to settle out of the reaction mixture. After 30 minutes, the solution was allowed to cool and the white precipitate was filtered off, washed with a little sodium dry benzene, then sodium dry ether. The product (12.458 g, 81%) was vacuum dried, and stored in the freezer. An analytical sample of 3-methoxy-5-phenyl-1,2-dithiolium fluorosulphonate (16) was prepared by crystallisation as white spars from acetonitrile, mp 110-112°.

Found: C 39.0; H 3.2

$C_{10}H_9FO_4S_3$ requires: C 39.0; H 2.9

^{1}H nmr spectrum (CF_3COOH): δ 4.69 (3H, OMe), 7.6-8.02 (5H, m, 5-Ph), 8.03 (1H, 4-H)

uv spectrum (methanol + 1% $HClO_4$): λ_{max} (nm) 325 sh ($\log \varepsilon$ 4.35) 291 (4.04), 208 (4.41)

The Reaction of 3-Substituted-5-phenyl-1,2-dithiolium Salts with Heterocyclic Amines

General Method:-

The amine (20 mM) was dissolved in ethanol (50 ml). The dithiolium salt (10 mM) was washed into the solution, with 10 ml ethanol, and the mixture refluxed for 10 minutes, allowed to cool, then poured into sodium carbonate solution (300 ml). This aqueous mixture was extracted with benzene (2 x 500 ml), the extracts washed with water (3 x 500 ml), dried and evaporated. Subsequent procedure is described for each reaction.

1. The Reaction of 3-Substituted-5-phenyl-1,2-dithiolium Salts with 2-Amino-2-thiazoline

(i) In Ethanol. 3-Chloro-5-phenyl-1,2-dithiolium chloride (2.496 g, 10 mM) and 2-amino-2-thiazoline (2.048 g, 20 mM) were used. The residue was chromatographed (50 x 2.8 cm, column I). Elution with petrol:benzene (3:1, 200 ml) gave pink eluates which were discarded. The second fraction (petrol:benzene, 2:1, 800 ml) gave orange eluates. The next 200 ml contained a mixture of the orange product and a colourless product.

Chromatography (30 x 2.0 cm, column II) of this mixture yielded the orange product in petrol:benzene (3:1, 200 ml), followed by the colourless product, in petrol:benzene (2:1, 200 ml and 1:1, 200 ml). The orange eluates were combined with fraction two of the first column, and the residual solid was recrystallised from cyclohexane to give 5-phenyl-1,2-dithiole-3-thione (11) (562 mg, 27%) as bronze plates, m.p. 125-126° (cf. lit.[164] 125-127°)

Found: C 51.1; H 2.9

Calc. for $C_9H_6S_3$: C 51.4; H 2.9

^{1}H nmr ($CDCl_3$): δ 7.41-7.73 (6H, m, 5-Ph + 4-H)

The next 500 ml of eluates (petrol:benzene, 1:1) from column I contained the colourless product. These were combined with the colourless compound from column II to give, after evaporation, 5-phenyl-1,2-dithiole-3-one (12) (416 mg, 21%) as cream coloured needles from cyclohexane, mp 115-117° (cf. lit.[164] 114-117°)

Found: C 55.4; H 3.0

Calc. for $C_9H_6S_2O$: C 55.6; H 3.1

^{1}H nmr ($CDCl_3$): δ 6.81 (1H, 4-H), 7.42-7.67 (5H, m, 5-Ph)

Further elution of column I with 550 ml benzene brought forth yellow eluates, which were impure. Rechromatography (20 x 2 cm) with benzene (300 ml) gave 2,3-dihydro-5-phenyl-1,3bλ^4,4-trithia-3a,7-diazacyclopent[a]pentalene (13) (91 mg, 3.3%) as yellow needles from cyclohexane, mp 126° (sharp).

Found: C 52.0; H 3.5; N 10.1; S 34.7

$C_{12}H_{10}N_2S_3$ requires: C 51.8; H 3.6; N 10.1; S 34.6

Accurate mass determination: 278.0008

$C_{12}H_{10}N_2S_3$ requires: 278.0006

^{1}H nmr ($CDCl_3$): δ 3.53 (2H, t, 2-H_2), 4.33 (2H, t, 3-H_2), 7.40-7.48 (3H, m, m- and p-protons of 5-Ph), 7.53 (1H, 6-H), 7.63-7.74 (2H, m, o-protons of 5-Ph)

uv spectrum: λ_{max} (nm) 387 ($\log\varepsilon$ 4.34), 284 (4.44), 235 sh (4.42) 211 (4.80)

Finally, column I was eluted with benzene:ether (9:1, 700 ml) which afforded an orange compound. The compound was rechromatographed on alumina (30 x 2 cm) using benzene:ether (9:1). 600 ml of eluant gave 2, 3-dihydro-5-phenyl-1, 6, 6aλ^4-trithia-3a, 7-diazacyclopent[a]pentalene (14) (99mg, 3.6%) as orange prisms from benzene, mp 202-203°.

Found: C 51.6; H 3.6; N 10.1; S 34.4

$C_{12}H_{10}N_2S_3$ requires: C 51.8; H 3.6; N 10.1; S 34.6

Accurate mass determination: 278.0000

$C_{12}H_{10}N_2S_3$ requires: 278.0006

^{1}H nmr (pyridine-D_5, saturated solution): δ 3.83 (2H, dt, 2-H_2), 4.38 (2H, dt, 3-H_2), 7.32-7.44 (3H, m, m- and p-protons of 5-Ph), 7.62 (1H, 4-H), 8.07-8.18 (2H, m, o-protons of 5-Ph)

uv spectrum (methanol): λ_{max} (nm) 417 (log ε 5.16), 321 (4.93), 279 (5.08), 233 (5.49), 205 sh (5.35)

(ii) In Acetonitrile. 3-Chloro-5-phenyl-1, 2-dithiolium chloride (2.492 g, 10 mM) and 2-amino-2-thiazoline (2.046 g, 20 mM) were used. Acetonitrile replaced ethanol, as solvent. The residue was chromatographed (50 x 2.7 cm, Laporte type H alumina, column I). Elution with benzene (500 ml), then benzene:ether (4:1, 500 ml) gave 5-phenyl-1, 2-dithiole-3-thione (11) (505 mg, 24%). Benzene:ether (1:1, 300 ml) brought forth a few mgs of 5-phenyl-1, 2-dithiole-3-one (12) (identified by tlc) which were discarded. Further elution with ether (600 ml) gave yellow eluates, which were impure. Chromatography (30 x 1.8 cm, silica) with benzene (950 ml) gave an impurity which was discarded. Benzene:ether (9:1, 500 ml; 4:1,

500 ml and 1:1, 500 ml) brought forth compound (13) (289 mg, 10.4%).

Further elution of column I gave impure compound (14). Successive chromatography on silica (20 x 1.8 cm) and Laporte type H alumina (40 x 1.8 cm) failed to purify this product. After chromatography, 42 mgs of impure material remained. Crystallisation did not purify this material.

(iii) In Hexamethylphosphoramide (HMPA). The following method was used:- To a solution of 2-amino-2-thiazoline (2.047 g, 20 mM) in HMPA (50 ml) was added 3-chloro-5-phenyl-1,2-dithiolium chloride (2.493 g, 10 mM). The salt was washed into the flask with 10 ml HMPA and the mixture was heated, with magnetic stirring, for 10 minutes, on an oil bath at 100°. After cooling, the mixture was poured into sodium carbonate solution (300 ml) and extracted with benzene (2 x 500 ml). The extracts were washed with water (9 x 500 ml), dried and evaporated. The residue was chromatographed (50 x 2.7 cm, column I). Petrol:benzene (2:1, 500 ml) gave impure 5-phenyl-1,2-dithiole-3-thione (11). Rechromatography (30 x 1.8 cm, petrol:benzene, 3:1) yielded 300 ml of impurities which were discarded, followed by a 750 ml fraction containing the product (326 mg, 15.5%).

Continued elution of column I with petrol:benzene (2:1, 500 ml) brought forth a trace of 5-phenyl-1,2-dithiole-3-one (12) (identified by tlc; impure). This fraction was discarded. Successive elution with petrol:benzene (1:1, 500 ml) and benzene (400 ml) gave only impurities. Finally, ether:benzene (19:1, 900 ml) gave

compound (14), in an impure state. Further chromatography (20 x 1.8 cm) of this compound, eluting with benzene (200 ml) then benzene:ether (19:1, 300 ml); and (40 x 1.8 cm) eluting with benzene (100 ml) followed by benzene:ether (19:1, 400 ml) failed to purify the compound completely. A pure sample (77 mg, 2.8%) was obtained by crystallisation from benzene.

(iv) In Ethanol. 3-Methoxy-5-phenyl-1,2-dithiolium fluorosulphonate (3.086 g, 10 mM) and 2-amino-2-thiazoline (2.044 g, 20 mM) were used. The rather insoluble residual solid was dissolved in warm benzene before chromatography (50 x 2.7 cm, column I). Elution with petrol:benzene (3:1) gave purple eluates (100 ml) which were discarded, followed by orange eluates (400 ml). The next fraction (petrol:benzene 2:1, 250 ml) contained the orange product and a colourless one. Chromatography (30 x 2.0 cm, column II) of this mixture gave the orange product in petrol:benzene (3:1, 150 ml) followed by the colourless one (petrol:benzene 1:1, 300 ml). The orange eluates were combined with fraction two of column I, giving 293 mg (13.9%) of the thione (11).

Continued elution of column I with 250 ml petrol:benzene (1:1) afforded the colourless product, which, combined with the colourless material from column II, gave the ketone (12) (359 mg, 18.5%).

Further elution with benzene (750 ml) and benzene:ether (9:1, 300 ml) provided no useful material. Finally, an impure sample of compound (14) was eluted in 800 ml benzene:ether (9:1).

Rechromatography (30 x 2.0 cm) with benzene:ether (9:1) brought forth 100 ml of solution, containing impure material (discarded) then 1000 ml of tlc pure eluates, giving 278 mg (10.3%) of product (14).

2. The Reaction of 3-Substituted-5-phenyl-1,2-dithiolium Salts with 2-Aminothiazole

(i) 2-Aminothiazole (2.006 g, 20 mM) and 3-chloro-5-phenyl-1,2-dithiolium chloride (2.495 g, 10 mM) were used. The residue was chromatographed (20 x 2.7 cm, column I). Elution with petrol:benzene (1:1, 250 ml) afforded a mixture of three products. The second fraction (benzene:ether, 9:1, 50 ml) consisted of an impure red product, which was discarded. Further elution with benzene:ether (9:1, 500 ml) gave red eluates, contaminated by polar impurities. Rechromatography (20 x 2.0 cm) of this fraction with petrol:benzene (1:2, 200 ml) gave pale yellow eluates which were discarded. Benzene:ether (9:1, 500 ml) afforded 5-phenyl-1,6,6aλ^4-trithia-3a,7-diazacyclopent[a]pentalene (20) (136 mg, 4.9%) as red plates from benzene, mp 180-182°.

Found: C 52.1; H 2.9; N 10.3

$C_{12}H_8N_2S_3$ requires: C 52.1; H 2.9; N 10.1

Accurate mass determination: 275.9845

$C_{12}H_8N_2S_3$ requires: 275.9850

^{1}H nmr (pyridine-D_5) saturated solution: δ 7.34-7.46 (4H, m, 2-H and m- and p-protons of 5-Ph), 8.08-8.20 (2H, m, o-protons of 5-Ph), 8.37 (1H, 4-H), 8.56 (1H, d, $J_{3,2}$=4.9 Hz, 3-H)

uv spectrum (methanol, qualitative): λ_{max} (nm) 447, 325, 279, 238, 204

Fraction one of column I was rechromatographed using "Camag" alumina, activity I (50 x 2.7 cm) to achieve a better separation of the close-running compounds. Elution with benzene:petrol (1:1, 2 l and 2:1, 200 ml) gave the thione (11) (173 mg, 82%). Benzene (200 ml) gave a mixture of the thione (11) and a yellow compound, which was discarded. Benzene:ether (9:1, 1500 ml and 5:1, 300 ml) gave a yellow compound, followed by a mixture of the yellow compound and the ketone (12). The mixture was discarded. The yellow compound was rechromatographed (40 x 2.0 cm). Elution with petrol:benzene (2:1, 500 ml) afforded 5-phenyl-1, 3bλ^4, 4-trithia-3a, 7-diazacyclopent[a]pentalene (19) (565 mg, 20%) as golden orange plates from cyclohexane, mp 165-167°.

Found: C 52.1; H 3.0; N 10.1

$C_{12}H_8N_2S_3$ requires: C 52.1; H 2.9; N 10.1

Accurate mass determination: 275.9858

$C_{12}H_8N_2S_3$ requires: 275.9850

^{1}H nmr ($CDCl_3$, saturated solution): δ7.08 (1H, d, $J_{2,3}$=3.9 Hz, 2-H), 7.45-7.53 (3H, m, m- and p-protons of 5-Ph), 7.48 (1H, 6-H), 7.62-7.76 (2H, m, o-protons of 5-Ph), 7.67 (1H, d, $J_{3,2}$=3.9Hz, 3-H).

uv spectrum: λ_{max} (nm) 430 sh (logε 4.13), 413 (4.19), 290 (4.23), 206 (4.43)

(ii) 2-Aminothiazole (2.002 g, 20 mM) and 3-methoxy-5-phenyl-1,2-dithiolium fluorosulphonate (3.085 g, 10 mM) were used. The residue was chromatographed (silica, 50 x 2.0 cm). Silica was

used, as it provided a better separation of the products from the impurities produced, in this particular case.

Elution with petrol:benzene (1:1, 950 ml) gave the thione (11), (308 mg, 14.6%). Benzene afforded 100 ml of impure eluates, which were discarded, followed by a 500 ml fraction containing product (19) and the ketone (12). Rechromatography of this fraction (40 x 2.0 cm) with petrol:benzene (3:1, 350 ml) gave a mixture of the ketone (12) and compound (19) (200 mg, discarded). More petrol:benzene (3:1, 350 ml and 1:1, 750 ml) provided principally the yellow product (19), which was recrystallised tlc pure from cyclohexane (464 mg, 16.8%).

No further useful material was obtained in the reaction.

3. The Reaction of 3-Substituted-5-phenyl-1,2-dithiolium Salts with Various 2-Aminopyridines

(i) 2-Aminopyridine (1.885 g, 20 mM) and 3-chloro-5-phenyl-1,2-dithiolium chloride (2.450 g, 10 mM) were used. Chromatography (50 x 2.7 cm, column I) of the residues, firstly with petrol:benzene (3:1) gave 50 ml of purple eluates which were discarded, followed by 900 ml of orange eluates. The third fraction (250 ml) contained a mixture of an orange and a colourless compound. Chromatography of this mixture (40 x 1.8 cm, column II) with petrol:benzene (4:1, 200 ml) afforded orange eluates; benzene (250 ml) gave colourless eluates. Combination of the orange eluates with fraction two of column I gave the thione (11) (141 mg, 6.7%).

The next 700 ml of eluates (petrol:benzene, 1:1) from column I contained the colourless product, which, when combined with the colourless eluates from column II gave the ketone (12) (647 mg, 33%). Further elution of column I (benzene, 800 ml) gave yellow eluates which were impure. Rechromatography (40 x 2.7 cm) with petrol:benzene (1:2, 100 ml) gave brown eluates which were discarded. Benzene (500 ml) gave 2-phenyl-1, 8bλ^4-dithia-4, 8a-diazacyclopent[a]indene (22a) (1.118 g, 41%) as yellow needles from cyclohexane, mp 133-133.5°.

Found: C 62.1; H 3.8; N 10.4

$C_{14}H_{10}N_2S_2$ requires: C 62.2; H 3.7; N 10.4

Accurate mass determination: 270.0295

$C_{14}H_{10}N_2S_2$ requires: 270.0285

^{1}H nmr ($CDCl_3$): δ 7.03 (1H, ddd, $J_{7,6}$ 7.6, $J_{7,8}$ 5.4, 7-H), 7.35-7.45 (4H, m, 5-H and m- and p-protons of 2-Ph), 7.61 (1H, 3H), 7.64-7.84 (3H, m, 6-H and o-protons of 2-Ph), 8.47 (1H, ddd, $J_{8,5}$ 0.9, $J_{8,7}$ 5.4, 8-H)

uv spectrum: λ_{max} (nm) 442 sh (log ε 3.83), 415 (4.17), 402 (4.17), 286 (4.21), 271sh (4.18), 230sh (4.29), 212 (4.52)

Finally, elution of column I with benzene:ether (4:1, 400 ml) gave impure orange eluates. Rechromatography (20 x 1.5 cm) using benzene:ether (9:1, 100 ml) gave 2-phenyl-1, 8aλ^4-dithia-3b, 8-diaza-cyclopent[a]indene (23a) (67mg, 2.5%) as a red tar.

Found: C 61.8; H 3.4; N 10.3

$C_{14}H_{10}N_2S_2$ requires: C 62.2; H 3.7; N 10.4

Accurate mass determination: 270.0295

$C_{14}H_{10}N_2S_2$ requires: 270.0285

(ii) 2-Amino-3-methylpyridine (2.163 g, 20 mM) and 3-chloro-5-phenyl-1,2-dithiolium chloride (2.494 g, 10 mM) were used. The residue was chromatographed (20 x 2.7 cm, column I). Petrol:benzene (4:1) gave 300 ml of orange eluates containing one orange compound, one yellow one and a trace of a colourless product. Fraction two (250 ml) contained the colourless product only. Elution with benzene (150 ml) brought forth pink and green eluates which were discarded. Further elution with benzene:ether (4:1, 200 ml) gave orange eluates. This fraction was rechromatographed (20 x 1.5 cm). Benzene (250 ml) gave 7-methyl-2-phenyl-1, 8aλ^4-dithia-3b, 8-diazacyclopent[a]indene (23b) (24 mg, 0.8%) as red prisms from benzene, mp 208-209°.

Found: C 63.2; H 4.0; N 9.8

$C_{15}H_{12}N_2S_2$ requires: C 63.3; H 4.3; N 9.8

Accurate mass determination: 284.0454

$C_{15}H_{12}N_2S_2$ requires: 284.0442

Fraction one of column I was rechromatographed (silica, 40 x 2.0 cm). Petrol:benzene (1:1, 500 ml) afforded the thione (11) (180 mg, 8.6%), followed by traces of three products which were discarded (400 ml). Benzene (100 ml) and benzene:ether (4:1, 350 ml) gave a mixture of 2 products. Rechromatography of the mixture (50 x 2.0 cm) with petrol:benzene (3:1, 600 ml) gave 5-methyl-2-phenyl-1, 8bλ^4-dithia-4, 8a-diazacyclopent[a]indene (22b) (399 mg, 14.0%) as yellow needles from cyclohexane, mp 110-110.3°.

Found: C 63.3; H 4.2; N 10.0

$C_{15}H_{12}N_2S_2$ requires: C 63.3; H 4.3; N 9.8

Accurate mass determination: 284.0440

$C_{15}H_{12}N_2S_2$ requires: 284.0442

^{1}H nmr ($CDCl_3$): δ 2.51 (3H, 5-Me), 6.97 (1H, dd, $J_{7,6}$ 7.8, $J_{7,8}$ 5.3, 7-H), 7.36-7.45 (3H, m, m- and p-protons of 2-Ph), 7.55 (1H, d, br, $J_{6,7}$ 7.8, 6-H), 7.67-7.80 (2H, m, o-protons of 2-Ph), 7.71 (1H, 3-H), 8.31 (1H, dd, br, $J_{8,7}$ 5.3; $J_{8,6}$ 1.6, 8-H)

uv spectrum: λ_{max} (nm) 444sh (logε 3.88), 419 (4.17), 407 (4.17), 287 (4.21), 269 (4.19), 230sh (4.29), 211 (4.52)

Elution with benzene (300 ml) yielded the colourless product, which was combined with fraction two of column I to give the ketone (12) (707 mg, 36%).

(iii) 2-Amino-4-methylpyridine (2.164 g, 20 mM) and 3-chloro-5-phenyl-1,2-dithiolium chloride (2.492 g, 10 mM) were used. The residue was chromatographed (50 x 2.7 cm). Elution with petrol:benzene (3:1, 100 ml) produced orange eluates. Petrol:benzene (2:1, 250 ml) gave a mixture of an orange and a colourless compound. Chromatography of this mixture (40 x 1.5 cm, column II) with petrol:benzene (4:1, 250 ml) afforded orange eluates; benzene (300 ml) gave colourless eluates. The orange eluates were combined with fraction one of column I to give the thione (11), (148 mg, 7.0%).

Elution of column I with petrol:benzene (1:1, 400 ml) afforded the colourless product. This was combined with the colourless eluates from column II, giving the ketone (12) (702 mg, 36%).

Continued elution of column I with petrol:benzene (1:1, 200 ml) afforded red eluates which were discarded; benzene (600 ml) gave

yellow eluates. Rechromatography of this fraction (40 x 2.0 cm) with benzene gave 50 ml of orange eluates which were discarded, then 400 ml of yellow eluates yielding 6-methyl-2-phenyl-1,8bλ^4-dithia-4,8a-diazacyclopent[a]indene (22c) (983 mg, 35%) as yellow needles from cyclohexane, mp 147.5-148°.

Found: C 63.2; H 4.2; N 9.9

$C_{15}H_{12}N_2S_2$ requires: C 63.3; H 4.3; N 9.8

Accurate mass determination: 284.0451

$C_{15}H_{12}N_2S_2$ requires: 284.0442

^{1}H nmr ($CDCl_3$): δ 2.37(3H, s,further split, $J_{6Me,5}$ 0.6, 6-Me), 6.89 (1H, dd, components further split, $J_{7,5}$ 1.6, $J_{7,8}$ 5.4, 7-H), 7.21 (1H, m, $J_{5,6Me}$ 0.6, $J_{5,7}$ 1.6, $J_{5,8}$ 0.8, 5-H), 7.37-7.48 (3H, m, m- and p-protons of 2-Ph), 7.59 (1H, 3H), 7.67-7.77 (2H, m, o-protons of 2-Ph), 8.34 (1H, d, br, $J_{8,5}$ 0.8, $J_{8,7}$ 5.4, 8-H)

uv spectrum: λ_{max} (nm) 442sh (logε 3.82), 414pl(4.17), 401 (4.17), 285 (5.24), 272sh(4.20), 230sh (4.36), 211 (4.60)

Finally, elution of column I with benzene:ether (3:1, 400 ml) gave orange eluates. Rechromatography (20 x 2.0 cm) with benzene gave 50 ml of yellow eluates which were discarded, then benzene:ether (9:1, 250 ml) gave orange eluates containing 6-methyl-2-phenyl-1,8aλ^4-dithia-3b,8-diazacyclopent[a]indene (23c) (18 mg, 0.6%) as orange microneedles from benzene, mp 187-189° with slow decomposition.

Found: C 63.4; H 4.2; N 9.7

$C_{15}H_{12}N_2S_2$ requires: C 63.3; H 4.3; N 9.8

Accurate mass determination: 284.0435

$C_{15}H_{12}N_2S_2$ requires: 284.0442

^1H nmr: see page 125

uv spectrum (methanol, qualitative): λ_{max} (nm) 457, 323, 279, 248, 213

(iv) 2-Amino-4-methylpyridine (2.162 g, 20 mM) and 3-methoxy-5-phenyl-1,2-dithiolium fluorosulphonate (3.082 g, 10 mM) were used. The residue was chromatographed. Chromatography was similar to that of (iii) above, giving thione (11) (518 mg, 25%); ketone (12) (481 mg, 25%) and compound (22c) (14.8%). Compound (22c) was purified by crystallisation from cyclohexane. The more polar product (23c) was not obtained.

(v) 2-Amino-5-methylpyridine (2.163 g, 20 mM) and 3-chloro-5-phenyl-1,2-dithiolium chloride (2.491g, 10 mM) were used. Chromatography (50 x 2.7 cm) column I) of the residue with petrol:benzene (3:1, 600 ml) gave orange eluates. Fraction two (250 ml) contained an orange and a colourless product. Rechromatography of this mixture (40 x 1.5 cm, column II) with petrol:benzene (4:1, 275 ml) gave orange eluates; benzene (250 ml) gave the colourless product. The orange eluates were combined with fraction one of column I to give the thione (11) (122 mg, 5.8%).

Elution of column I with benzene (450 ml) gave a colourless compound, which, combined with the colourless eluates from column II afforded the ketone (12) (866 mg, 44%). Benzene (100 ml) and benzene:ether (9:1, 150 ml) gave brown eluates which were discarded. Benzene:ether (9:1, 500 ml) gave a yellow compound

contaminated with brown and blue impurities. Rechromatography of this mixture (40 x 2.0 cm) with petrol:benzene (2:1) gave 150 ml of brown eluates which were discarded, then 2000 ml of yellow eluates, and 200 ml of eluates containing a yellow and a blue compound. The yellow eluates afforded 7-methyl-2-phenyl-1, 8bλ^4-dithia-4, 8a-diazacyclopent[a]indene (22d) (696 mg, 25%) as yellow pyramids from cyclohexane, mp 163-164°.

Found: C 63.5; H 4.4; N 9.9

$C_{15}H_{12}N_2S_2$ requires: C 63.3; H 4.3; N 9.8

Accurate mass determination: 284.0448

$C_{15}H_{12}N_2S_2$ requires: 284.0442

^{1}H nmr ($CDCl_3$): δ 2.32 (3H, br, 7-Me), 7.35-7.76 (7H, m, 2-Ph and 5-H and 6-H), 7.58 (1H, 3-H), 8.30 (1H, further split, 8-H)

uv spectrum: λ_{max} (nm) 444sh (log ε3.82), 416sh. (4.16), 404 (4.18), 284 (4.24), 273sh (4.23), 231sh (4.31), 213 (4.51).

Further elution of column I (benzene:ether, 4:1, 300 ml) gave orange eluates. Rechromatography (20 x 1.5 cm) with benzene (50 ml) gave yellow eluates which were discarded; benzene:ether (9:1, 200 ml) gave 5-methyl-2-phenyl-1, 8aλ^4-dithia-3b, 8-diazacyclopent[a]indene (23d) (6 mg, 0.2%) as red needles from cyclohexane and benzene, mp 191-192°.

Found: C 63.6; H 4.2; N 9.8

$C_{15}H_{12}N_2S_2$ requires: C 63.3; H 4.3; N 9.8

Accurate mass determination: 284.0440

$C_{15}H_{12}N_2S_2$ requires: 284.0442

(vi) 2-Amino-6-methylpyridine (2.166 g, 20 mM) and 3-chloro-5-phenyl-1,2-dithiolium chloride (2.497 g, 10 mM) were used. The residue was chromatographed (50 x 2.7 cm, column I). Petrol:benzene (3:1) afforded orange eluates (800 ml), followed by 150 ml of eluates containing an orange and a colourless compound. Rechromatography of this mixture (40 x 1.5 cm, column II) with petrol:benzene (4:1, 230 ml) gave orange eluates; benzene (250 ml) gave the colourless compound. Combination of the orange eluates with fraction one of column I gave the thione (11) (147 mg, 7.0%).

Elution of column I with benzene (500 ml) afforded a colourless compound, which was combined with the colourless eluates from column II to give the ketone (12) (477 mg, 25%). Benzene (300 ml) yielded brown eluates which were discarded. Benzene:ether (9:1, 550 ml) gave yellow eluates, contaminated with brown and blue impurities. Rechromatography of this mixture (40 x 2.0 cm, column III) with petrol:benzene (2:1) gave 100 ml of brown solution which was discarded, then 200 ml of brown eluates containing some of the yellow product, then 1800 ml of yellow eluates (tlc pure), and finally 200 ml of yellow eluates containing some of the blue compound. The impure yellow fractions were rechromatographed (40 x 2 cm, column IV). Petrol:benzene (2:1) gave 400 ml of mainly brown impurities (129 mg) which were discarded, then 1200 ml of tlc pure yellow eluates. Combination of the pure yellow material from columns III and IV afforded 8-methyl-2-phenyl-1,8bλ^4-dithia-4,8a-diazacylopent[a]indene (22e) (766 mg, 27%) as yellow spars from cyclohexane, mp 118.5-119°.

Found: C 63.2; H 4.3; N 9.9

$C_{15}H_{12}N_2S_2$ requires: C 63.3; H 4.3; N 9.8

Accurate mass determination: 284.0432

$C_{15}H_{12}N_2S_2$ requires: 284.0442

^1H nmr ($CDCl_3$): δ 2.69 (3H, 8-Me), 6.92 (1H, d, components further split, $J_{7,6}$ 7.4, $J_{7,5}$ 1.0, 7-H), 7.30 (1H, d, components further split, $J_{5,6}$ 8.5, $J_{5,7}$ 1.0, 5-H), 7.41-7.52 (3H, m, m- and p-protons of 2-Ph), 7.63-7.82 (3H, m, o-protons of 2-Ph, and 6-H), 7.67 (1H, 3-H).

uv spectrum: λ_{max} (nm) 444 sh (log ε 3.86), 415pl (4.17), 404 (4.17), 288 (4.23), 270 (4.20), 230sh (4.31), 212 (4.54)

No further useful material was obtained from column I.

(vii) 2-Amino-4,6-dimethylpyridine (2.444 g, 20 mM) and 3-chloro-5-phenyl-1,2-dithiolium chloride (2.492 g, 10 mM) were used. The residue was chromatographed (50 x 2.7 cm, column I). Petrol:benzene (3:1) afforded orange eluates (700 ml) followed by 250 ml of eluates containing an orange and a colourless product. Rechromatography of this mixture (40 x 1.5 cm, column II) with petrol:benzene (4:1, 200 ml) gave orange eluates; benzene (250 ml) yielded the colourless compound. The orange eluates from column II were combined with fraction one of column I to give the thione (11) (136 mg, 6.5%).

Elution of column I with benzene (400 ml) afforded a colourless compound, which was combined with the colourless eluates from column II to give the ketone (12) (797 mg, 41%). Benzene (100 ml) gave red/brown eluates which were discarded.

More benzene (850 ml) gave a yellow product which was contaminated with a faster-running brown impurity, and a more polar blue one. This mixture was purified by extracting the majority of the brown material out, with petrol. The remaining yellow material was rechromatographed (40 x 2.0 cm). Petrol:benzene (1:1, 1400 ml) gave tlc pure 6, 8-dimethyl-2-phenyl-1, 8bλ^4-dithia-4, 8a-diazacylopent[a]indene (22f) (797mg, 26%) as yellow microspars from cyclohexane, mp 120-120.5°.

Found: C 64.4; H 4.4; N 9.2

$C_{16}H_{14}N_2S_2$ requires: C 64.4; H 4.7; N 9.4

Accurate mass determination: 298.0607

$C_{16}H_{14}N_2S_2$ requires: 298.0598

^{1}H nmr ($CDCl_3$): δ 2.32 (3H, 6-Me), 2.59 (3H, 8-Me), 6.69 (1H, br, $J_{7,5}$ 1.5, 7-H), 7.03 (1H, br, $J_{5,7}$ 1.5, 5-H), 7.35-7.46 (3H, m, m- and p-protons of 2-Ph), 7.59 (1H, 3H), 7.65-7.77 (2H, m, o-protons of 2-Ph)

uv spectrum: λ_{max} (nm) 444 sh (log ε 3.84), 416sh (4.16), 405 (4.17), 287 (4.23), 272 (4.20), 230sh (4.35), 214 (4.56)

No further useful material was obtained from column I.

4. The Reaction of 3-Chloro-5-phenyl-1, 2-dithiolium Chloride with 4-Aminopyridine

4-Aminopyridine (1.884 g, 20 mM) and 3-chloro-5-phenyl-1, 2-dithiolium chloride (2.492 g, 10 mM) were used. The reaction mixture was very dirty. Chromatography (50 x 2.7 cm, column I) of the residue with petrol:benzene (3:1) gave 950 ml of orange eluates. The next 300 ml contained an orange product and a

colourless one. Rechromatography (40 x 1.5 cm, column II) of this mixture with petrol:benzene (4:1, 250 ml) gave orange eluates; benzene (250 ml) gave a colourless product. The orange eluates were combined with the orange eluates from column I to give the thione (11) (242 mg, 11.5%).

Elution of column I with benzene (600 ml) afforded a colourless compound which was combined with the colourless eluates from column II to give the ketone (12) (811 mg, 42%). Further elution with benzene:ether (1:1) and ether gave no useful material. Ether:methanol (49:1, 500 ml) gave a yellow product, contaminated by brown impurities. Rechromatography (15 x 1.5 cm) with benzene and benzene:ether (4:1) brought off some impurities. The product was obtained, impure, in 500 ml of benzene:ether (1:1). Rechromatography (silica, 15 x 1.5 cm) with benzene, then benzene:ether (1:1) gave no useful material. Ether (200 ml) gave yellow eluates containing 5-phenyl-3-(4-pyridylimino)-3H-1,2-dithiole (24) (24 mg, 0.9%) as yellow plates from cyclohexane, mp 168.5-169.5°.

Found: C 62.3; H 3.6; N 10.2

$C_{14}H_{10}N_2S_2$ requires: C 62.2; H 3.7; N 10.4

Accurate mass determination: 270.0271

$C_{14}H_{10}N_2S_2$ requires: 270.0285

uv spectrum (qualitative): λ_{max} (nm) 362, 273, 213

5. The Reaction of 3-Chloro-5-phenyl-1,2-dithiolium Chloride with 2-Aminopyrimidine

2-Aminopyrimidine (1.904 g, 20 mM) and 3-chloro-5-phenyl-1,2-dithiolium chloride (2.491 g, 10 mM) were used. The residue was chromatographed (50 x 2.7 cm, column I). Petrol:benzene (3:1, 650 ml) gave orange eluates. The next 250 ml of eluates was a mixture of an orange and a colourless product. Rechromatography (40 x 1.5 cm, column II) with petrol:benzene (4:1, 250 ml) gave orange eluates; benzene (250 ml) gave a colourless product. Combination of the orange eluates from columns I and II afforded the thione (11) (158 mg, 7.5%).

Elution of column I with benzene (700 ml) gave colourless eluates, which, when combined with the colourless product from column II, gave the ketone (12) (843 mg, 43%). Elution with ether and ether:methanol (19:1) brought forth blue and pink eluates, which were discarded. Ether:methanol (4:1, 500 ml) gave yellow eluates. Rechromatography (10 x 1.5 cm) with ether removed impurities, and ether:methanol (19:1, 350 ml) gave 2-phenyl-1,8bλ^4-dithia-4,5,8a-triazacyclopent[a]indene (25) (113 mg, 4.2%) as yellow microprisms from methanol/benzene, mp 169-171°.

Found: C 57.8; H 3.2; N 15.7

$C_{13}H_9N_3S_2$ requires: C 57.5; H 3.3; N 15.5

Accurate mass determination: 271.0245

$C_{13}H_9N_3S_2$ requires: 271.0238

^{1}H nmr ($CDCl_3$): δ 7.02 (1H, t, poorly resolved, 7-H), 7.40-7.53 (3H, m, m- and p-protons of 2-Ph), 7.64-7.77 (3H, m, o-protons of 2-Ph, and 3-H), 8.80 (2H, vbr, 6-H and 8-H).

^{1}H nmr ($CDCl_3$, -24°C): δ 7.05 (1H, t, $J_{7,6(7,8)}$ 4.8, 7-H), 7.44-7.54 (3H, m, m- and p-protons of 2-Ph), 7.66-7.76 (3H, m, o-protons of 2-Ph and 3-H), 8.81 (2H, d, $J_{6,7(8,7)}$ 4.8, 6- and 8-H)

uv spectrum: λ_{max} (nm) 4.25sh (log ε 3.87), 406 (4.18), 394sh (4.16), 291 (4.21), 225sh (4.36), 210 (4.41)

6. The Reaction of 3-Chloro-5-phenyl-1,2-dithiolium Chloride with 2,6-Diaminopyridine

2,6-Diaminopyridine (2.181 g, 20 mM) and 3-chloro-5-phenyl-1,2-dithiolium chloride (2.495 g, 10 mM) were used. The residue, which was dark brown and contained black scum, was chromatographed (20 x 2.7 cm, column I). Elution with benzene (300 ml) afforded a mixture of an orange and a colourless compound. Rechromatography (50 x 2.0 cm) of this mixture with petrol:benzene (3:1, 700 ml) gave the thione (11) (296 mg, 14.1%), benzene (300 ml) gave the ketone (12) (170 mg, 8.8%).

Elution of column I with benzene:ether (9:1, 400 ml) brought forth yellow eluates with an orange tail. This mixture was also rechromatographed (50 x 2.0 cm). Benzene:ether (9:1) gave 1000 ml of bright orange eluates which afforded 8-(5-phenyl-1,2-dithiol-3-ylideneamino)-2-phenyl-1, 8bλ^4-dithia-4, 8a-diazacyclopent[a]indene (29) (181 mg, 4.3%) as marigold orange plates from benzene, mp 191-192°.

Found: C 59.8; H 3.4; N 9.1

$C_{23}H_{15}N_3S_4$ requires: C 59.8; H 3.3; N 9.1

Accurate mass determination: 461.0018

$C_{23}H_{15}N_3S_4$ requires: 461.0149

^1H nmr: - see Table 2.

uv spectrum (methanol, qualitative): λ_{max} (nm) 399, 291, 210.

Elution of column I with ether:methanol (4:1, 750 ml) brought forth a pink compound. Rechromatography (15 x 3.5 cm) with ether:methanol (5:2, 1 l.) gave 4-(5-phenyl-1,2-dithiol-3-ylidene-amino)-2-phenyl-1,8aλ^4-dithia-3b,8-diazacyclopent[a]indene (31), (136 mg, 4.9%) as red rods from benzene, mp 286-288°.

Found: C 60.1; H 3.0; N 8.8

$C_{23}H_{15}N_3S_4$ requires: C 59.8; H 3.3; N 9.1

Accurate mass determination: 461.0129

$C_{23}H_{15}N_3S_4$ requires: 461.0149

^1H nmr: A satisfactory spectrum was not obtained due to the insoluble nature of the product.

uv spectrum (methanol, qualitative): λ_{max} (nm) 500, 334, 288, 225.

7. <u>The Reaction of 3-Chloro-5-phenyl-1,2-dithiolium Chloride with 2-Aminobenzimidazole</u>

2-Aminobenzimidazole (2.664 g, 20 mM) and 3-chloro-5-phenyl-1,2-dithiolium chloride (2.493 g, 10 mM) were used. The residue was chromatographed (15 x 2.0 cm, column I). The residue was dissolved in 700 ml of warm benzene, which was passed through the column, followed by 300 ml of cold benzene. These eluates contained a mixture of an orange compound, and a colourless product. Rechromatography (50 x 2.7 cm) of this mixture with

petrol:benzene (3:1, 900 ml) gave the thione (11) (225 mg, 10.1%); benzene (500 ml) gave the ketone (12) (786 mg, 40%).

Further elution of column I with benzene:ether (1:1) and ether afforded no useful material. Ether:methanol (99:1, 250 ml) gave orange/yellow eluates, which contained 2-phenyl-1,9cλ^4-dithia-4,5,9b-triaza-5H-pentaleno[1,2-a]indene (33). The compound was recrystallised by dissolving it in hot acetone, then adding benzene. The acetone was boiled off, and the compound crystallised from the benzene as orange microprisms (108 mg, 3.5%), mp 288-290° (with sublimation from 230°).

Found: C 61.9; H 3.6; N 13.5

$C_{16}H_{11}N_3S_2$ requires: C 62.1; H 3.6; N 13.6

Accurate mass determination: 309.0380

$C_{16}H_{11}N_3S_2$ requires: 309.0394

^{1}H nmr (DMSO-D_6, saturated solution): δ 7.10-7.23 (2H, m, 6- and 9-H), 7.35-7.63 (5H, m, 2-Ph), 7.78 (1H, 3-H), 7.79-7.90 (2H, m, br, 7- and 8-H), 12.38 (1H, br, NH).

uv spectrum (methanol): λ_{max} (nm) 414 (logε 4.30), 295 (4.32), 225sh (4.42), 212 (4.63)

8. The Reaction of 3-Chloro-5-phenyl-1,2-dithiolium Chloride with 2-Methylpyridine

2-Methylpyridine (1.862 g, 20 mM) and 3-chloro-5-phenyl-1,2-dithiolium chloride (2.494 g, 10 mM) were used. Excess 2-methylpyridine was removed azeotropically, at reduced pressure, with xylene. The residue was chromatographed (50 x 2.7 cm, column I). Petrol:benzene (3:1) afforded 1000 ml of orange eluates, followed

by 400 ml of a mixture of an orange and a colourless product. Rechromatography (40 x 1.5 cm, column II) of the mixture with petrol:benzene (4:1, 350 ml) gave orange eluates; benzene (300 ml) afforded a colourless product. The orange eluates were combined with the first fraction of column I to give the thione (11) (246 mg, 11.7%).

Elution of column I with benzene (500 ml) afforded a colourless compound which was combined with the colourless eluates from column II to give the ketone (12) (810 mg, 42%).

Further elution of column I with benzene:ether (1:1), ether, and ether:methanol (4:1) gave no useful material. Ether:methanol (1:1, 500 ml) afforded purple eluates which decomposed rapidly during attempts to purify them.

9. The Reaction of 3-Chloro-5-phenyl-1,2-dithiolium Chloride with N-Phenylbenzamidine

Preparation of Amidines. N-Phenylbenzamidine was prepared using the established procedure[167]. Attempts to prepare N-phenylacetamidine, using Weintraub's general method[168] for the preparation of amidines, proved fruitless. An attempt to prepare acetamidine by neutralisation of its hydrochloride salt using sodium carbonate or sodium hydroxide was unsuccessful. In both cases, the amide was obtained instead.

N-Phenylbenzamidine (3.925 g, 20 mM) reacted with 3-chloro-5-phenyl-1,2-dithiolium chloride (2.492 g, 10 mM). The residue was chromatographed (50 x 2.7 cm, column I). Petrol:benzene (4:1)

gave 600 ml of orange eluates followed by 200 ml of a mixture of an orange and a colourless product. Rechromatography of this mixture (40 x 1.5 cm, column II) with petrol:benzene (4:1, 250 ml) gave orange eluates; benzene (250 ml) gave a colourless product. The orange eluates were combined with the orange eluates from column I, to give the thione (11) (147 mg, 7.0%).

Elution of column I with benzene (500 ml) gave colourless eluates, which, when combined with the colourless product from column II, afforded the ketone (12) (843 mg, 43%).

Continued elution of column I with benzene:ether (4:1, 250 ml) afforded brown eluates which were discarded. Benzene:ether (1:1, 400 ml) gave orange eluates. Rechromatography (20 x 1.5 cm) with benzene:ether (1:1, 250 ml) afforded 5-phenyl-3-phenylimino-3H-1,2-dithiole (46) (17 mg, 0.6 %) as dark yellow microprisms from benzene, mp 130-132° (lit.[154,155] 131.5°).

Accurate mass determination: 269.0343

Calc. for $C_{15}H_{11}NS_2$: 269.0333

B. SYNTHESIS OF 6-METHYL-2-PHENYL-1,8aλ^4-DITHIA-3b,8-DIAZACYCLOPENT[a]INDENE AND ATTEMPTED SYNTHESIS OF 1,6,6aλ^4-TRITHIA-3a,7-DIAZACYCLOPENT[a]PENTALENES

1. Preparation of 2-Trichloromethylsulphenamidoheterocycles

(i) 2-Trichloromethylsulphenamido-4-methylpyridine (54)

The following adaption of Goerdeler's method[102] was used:-

Solutions of 2-amino-4-methylpyridine (10.81 g, 100 mM) in ether (150 ml), perchloromethyl mercaptan (18.57 g, 10.95 ml, 100 mM) in ether (60 ml) and sodium carbonate (10.60 g, 100 mM) in water (100 ml) were simultaneously added, with mechanical stirring, to 600 ml of ether which had been cooled to approx. 0°. A little of the perchloromethyl mercaptan was added first. After one hour, the layers were separated, and the ether layer was washed with water (x 4), dried and evaporated at reduced pressure on a cold water bath. The resulting solid was washed with petrol and was sufficiently pure for further use. 13.27 g (52%) of product was obtained. A small portion was recrystallised for characterisation. 2-Trichloromethylsulphenamido-4-methylpyridine (54) crystallised as white rods from diethyl ether, mp 118.5-120°, with decomposition.

Found: C 32.5; H 2.6; N 10.7

$C_7H_7Cl_3N_2S$ requires: C 32.6; H 2.7; N 10.9

Accurate mass determination: 255.9406

$C_7H_7Cl_3N_2S$ requires: 255.9386

^1H nmr ($CDCl_3$, saturated solution): δ 2.33 (3H, br, 4-Me), 6.72

(1H, d, $J_{5,6}$ 5.0, 5-H), 7.25 (1H, br, 3H), 8.08 (1H, d, $J_{6,5}$ 5.0, 6-H).

(ii) 2-Trichloromethylsulphenamidothiazole (52)

2-Aminothiazole (10.01 g, 100 mM) was used in the above method, and gave the product (52) in 52% yield, mp 55-60° (lit.[104] 53-59°).

(iii) 2-Trichloromethylsulphenamido-4,5-dihydrothiazole (53)

To a solution of 2-amino-2-thiazoline (2.043 g, 20 mM) in tetrahydrofuran (50 ml) was added dropwise, with stirring, a solution of perchloromethyl mercaptan (1.859 g, 1.20 ml, 10 mM) in tetrahydrofuran (10 ml). After 30 minutes the precipitate was filtered off and washed with water. The remaining solid was combined with the tetrahydrofuran filtrates, which were then evaporated to give 2-trichloromethylsulphenamido-4,5-dihydrothiazole (53), as a tarry white solid. The compound was not purified further because of its instability. It was stored in the freezer. The product was characterised by its mass spectrum, M^+ at 250.

2. Reaction of Benzoylacetic Acid with 2-Trichloromethylsulphenamidoheterocycles

Benzoylacetic acid was prepared by the method of Levine and Hauser[169].

(i) Reaction with 2-Trichloromethylsulphenamido-4-methylpyridine (54)

To a solution of benzoylacetic acid (4.105 g, 25 mM) in dimethylformamide (200 ml) was added triethylamine (15.18 g,

20.85 ml, 150 mM) followed by the sulphenamide (6.440 g, 25 mM) which was rinsed into the flask with more dimethylformamide (50 ml). The mixture was stirred for one hour, poured into water, and extracted twice with benzene. The extracts were washed with water (x 6) dried and evaporated. The residue was chromatographed (30 x 2.7 cm, column I). Benzene (650 ml) gave pale yellow eluates containing a mixture of three products. Comparative tlc established that two of the products were acetophenone, and 7-methyl-3-(4-methyl-2-pyridylimino)-3H-[1,2,4]-thiadiazolo[4,3-a]pyridine (58). The mixture was rechromatographed (60 x 2.7 cm) with petrol:benzene (1:1, 250 ml) giving yellow eluates, which were discarded. Petrol:benzene (1:1, 250 ml and 1:2, 300 ml) and benzene (900 ml) afforded a colourless product. Recrystallisation from cyclohexane gave 7-methyl-3H-[1,2,4]thiadiazolo[4,3-a]pyridine-3-one (57, X=O) (2.018 g, 49%) as white spars, mp 124-125.5°.

Found: C 50.8; H 3.4; N 17.0

Calc. for $C_7H_6N_2OS$: C 50.6; H 3.6; N 16.9

Accurate mass determination: 166.0203

Calc. for $C_7H_6N_2OS$: 166.0201

^1H nmr ($CDCl_3$): δ 2.30 (3H, d, further split, $J_{7\text{-Me},8}$ 1.3, 7-Me), 6.40 (1H, dd, $J_{6,5}$ 7.2, $J_{6,8}$ 1.6, 6-H), 6.87 (1H, m, $J_{8,6}$ 1.6, $J_{8,7\text{-Me}}$ 1.3, 8-H), 7.71 (1H, d, br, $J_{5,6}$ 7.2, 5-H).

Elution of column I with benzene:ether (4:1) gave a yellow solution which was discarded. Ether (800 ml) gave a yellow compound. Rechromatography (20 x 2.7 cm) with ether afforded

6-methyl-2-phenyl-1-oxa-8aλ^4-thia-3b,8-diazacyclopent[a]indene (56) (551 mg, 8.2%) as yellow platelets from benzene, mp 240-241°.

Found: C 67.1; H 4.4; N 10.4

$C_{15}H_{12}N_2OS$ requires: C 67.1; H 4.5; N 10.4

Accurate mass determination: 268.0657

$C_{15}H_{12}N_2OS$ requires: 268.0670

^{1}H nmr (pyridine-D_5, 80°C, saturated solution): δ 2.07 (3H, d, $J_{6\text{-Me},7}$ 1.3, 6-Me), 6.38 (1H, dd, $J_{5,4}$ 6.3, $J_{5,7}$ 1.7, 5-H), 6.98 (1H, m, $J_{7,5}$ 1.7, $J_{7,6\text{-Me}}$ 1.3, 7-H), 7.32-7.47 (3H, m, m- and p-protons of 2-Ph), 8.11-8.24 (3H, m, o-protons of 2-Ph, and 4-H)

uv spectrum (methanol): λ_{max} (nm) 409 (logε4.31), 366sh (3.93) 239sh (4.27), 226 (4.35), 206 (4.19)

(ii) Reaction with 2-Trichloromethylsulphenamidothiazole (52)

To a solution of benzoylacetic acid (825 mg, 5 mM) in dimethylformamide (40 ml) was added triethylamine (2.53 g, 3.5 ml, 25 mM) and the sulphenamide (52) (1.248 g, 5 mM) which was rinsed into the flask with more dimethylformamide (10 ml). The mixture was stirred for one hour, poured into water and extracted three times with benzene. The extracts were washed with water (x 6) dried and evaporated. Chromatography of the residue (30 x 2.0 cm) with benzene gave acetophenone which was discarded. Benzene:ether (9:1, 200 ml) afforded pale yellow eluates which contained 16 mg of an impure yellow product with M^+ at 260. This was tentatively identified as 5-phenyl-6-oxa-6aλ^4-thia-3a,7-diazacyclopent[a]-pentalene (55).

(iii) Reaction with 2-Trichloromethylsulphenamido-4,5-dihydrothiazole (53)

The method of (ii) above was used, with 2-trichloromethylsulphenamido-4,5-dihydrothiazole (1.258 g, 5 mM). No useful material was obtained from the reaction.

The reaction was repeated under stronger conditions:- A solution of benzoylacetic acid (825 mg, 5 mM) and sodium hydroxide (200 mg, 5 mM) in ethanol (25 ml) was added dropwise to a solution of 2-trichloromethylsulphenamido-4,5-dihydrothiazole (53) (1.258 g, 5mM) in ethanol (100 ml) in the presence of excess sodium carbonate. The solution was stirred for 24 hours, poured into water and extracted with ether. The two phases were worked up separately.

The aqueous phase was acidified with dilute hydrochloric acid, extracted twice with ether and the extracts washed with water (x 3) dried and evaporated. No useful material was obtained.

The organic phase was washed with water (x 3) dried and evaporated. Chromatography (30 x 2.0 cm) did not yield any of the desired product.

3. Thionation of 6-Methyl-2-phenyl-1-oxa-8aλ^4-thia-3b,8-diazacyclopent[a]indene (56)

6-Methyl-2-phenyl-1-oxa-8aλ^4-thia-3b,8-diazacyclopent[a]indene (268 mg, 1 mM) was dissolved in dry pyridine (20 ml). Phosphorus pentasulphide (444 mg, 2 mM) was rinsed in, with pyridine (5 ml). The mixture was refluxed for one hour, allowed to cool, poured into water (500 ml) and extracted with

benzene (3 x 250 ml). The extracts were washed with water (3 x 250 ml) dried and evaporated. The residue was chromatographed (25 x 2.0 cm). Benzene (300 ml) gave 5-phenyl-1,2-dithiole-3-thione (11) (10 mg, 0.5%), mp 125-126°, mixed mp 125-126.5°, M^+=210. Benzene:ether (3:1, 600 ml) gave 6-methyl-2-phenyl-1, 8aλ^4-dithia-3b, 8-diazacyclopent[a]indene (23c) (41 mg, 1.4%) as orange microneedles from benzene/cyclohexane, mp 187-188.5°, mixed mp 187-188.5° M^+=284.

^{1}H nmr (pyridine-D_5, saturated solution): δ 2.16 (3H, d, $J_{6Me,7}$ 1.3, 6-Me), 6.66 (1H, dd, $J_{5,4}$ 7.5, $J_{5,7}$ 1.9, 5-H), 7.24 (1H, m, 7-H), 7.32-7.46 (3H, m, m- and p-protons of 2-Ph), 8.17-8.28 (2H, m, o-protons of 2-Ph), 8.45 (1H, 3-H), 8.82 (1H, d, $J_{4,5}$ 7.5Hz, 4-H)

Ether:methanol (99:1, 600 ml) afforded unchanged starting material (56) (207 mg, 77%).

4. Preparation of 7-Methyl-3-(4-methyl-2-pyridylimino)-3H-[1,2,4]thiadiazolo[4,3-a]pyridine (58)

Pott's method[100] was used. The product was chromatographed (20 x 2.0 cm). Elution with benzene afforded 7-methyl-3-(4-methyl-2-pyridylimino)-3H-[1,2,4]thiadiazolo[4,3a]pyridine (58), as yellow prisms from benzene, mp 192-194° (lit.[100] 189-191°, orange needles).

Found: C 60.9; H 4.6; N 22.2

Calc. for $C_{13}H_{12}N_4S$: C 60.9; H 4.7; N 21.9

C. SYNTHESIS OF 1H and 6H-TRIHETERAPENTALENES

Preparation of Starting Materials

5-Amino-3-methyl-1,2,4-thiadiazole (72) and 5-amino-3-methylthio-1,2,4-thiadiazole (64) were prepared by the methods of Goerdeler[170,171]. 5-Amino-3-methyl-1,2,4-thiadiazole was converted to 5-amino-3,4-dimethyl-4H-1,2,4-thiadiazolium iodide (65a) and thence to 4,5-dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole (66a) using the established procedure[107].

Preparation of 5-Amino-4-methyl-3-methylthio-4H-1,2,4-thiadiazolium Iodide (65b)

Methyl iodide (85.16 g, 37.35 ml, 600 mM) was added to a solution of 5-amino-3-methylthio-1,2,4-thiadiazole (29.44 g, 200 mM) in ethanol (100 ml). The mixture was refluxed for 18 hours, then cooled in an ice-salt bath. The pale yellow product was filtered off, washed with acetone and then ether. A further amount of product was obtained by treating the mother liquors with ether, and filtering off the precipitate, total yield (35.35 g, 61%). A sample of 5-amino-4-methyl-3-methylthio-4H-1,2,4-thiadiazolium iodide (65b) was recrystallised as white spars from methanol, mp 207-210°.

Found: C 16.7; H 2.9; N 14.4

$C_4H_8IN_3S_2$ requires: C 16.6; H 2.8; N 14.5

^{1}H nmr (DMSO-D_6): δ 2.70 (3H, 3-SMe), 3.56 (3H, 4-Me), 10.00 (2H, br, NH_2)

Preparation of 4,5-Dihydro-5-imino-4-methyl-3-methylthio-1,2,4-thiadiazole (66b)

A solution of sodium hydroxide (2.00 g, 50 mM), in water (100 ml) was added to a solution of 5-amino-4-methyl-3-methylthio-4H-1,2,4-thiadiazolium iodide (14.46 g, 50 mM) in water (200 ml). The aqueous solution was stirred for a few minutes, then extracted with benzene (2 x 500 ml). The extracts were washed with water (x 3) dried and evaporated to give 4,5-dihydro-5-imino-4-methyl-3-methylthio-1,2,4-thiadiazole (66b) (7.754 g, 96%) as a colourless oil which was stored under refrigeration. The product was sufficiently pure for further use.

Accurate mass determination: 161.0071

$C_4H_7N_3S_2$ requires: 161.0081

^1H nmr ($CDCl_3$): δ 2.55 (3H, 3-SMe), 3.23 (3H, 4-Me), 6.92 (1H, br, =NH)

1. Synthesis of Thiaazapentalenes

a. Synthesis of 3,5,6-Trisubstituted-6H-3aλ^4-thia-1,2,3,4,6-pentaazapentalenes

General Method:-

The relevant 5-imino-1,2,4-thiadiazole (10 mM) was dissolved in acetonitrile:pyridine (19:1, 100 ml). Arenediazonium fluoroborate (40 mM) was added, and the mixture was stirred at room temperature. The reaction mixture was poured into water,

then extracted with benzene (x2). The extracts were washed with water (x 3) dried and evaporated. Subsequent procedure is described for each individual case.

(i) The residue from 4,5-dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole (1.292 g, 10 mM) and benzenediazonium fluoroborate (7.677 g, 40 mM) was chromatographed (40 x 2.7 cm). Benzene and benzene:ether (3:1 and 1:1) gave pale yellow eluates which were discarded. Ether gave yellow eluates which were rechromatographed (40 x 2 cm). Elution with ether gave 5,6-dimethyl-3-phenyl-6H-3aλ^4-thia-1,2,3,4,6-pentaazapentalene (67a) (197 mg, 8.4%) as yellow microspars from cyclohexane, mp 190-192°.

Found: C 51.3; H 4.7; N 30.2

$C_{10}H_{11}N_5S$ requires: C 51.5; H 4.7; N 30.0

Accurate mass determination: 233.0723

$C_{10}H_{11}N_5S$ requires: 233.0735

^1H nmr: see Table 4

uv spectrum: λ_{max} (nm) 352 (log ε 4.06), 332sh (3.98), 263 (3.54), 224 (4.14), 213 (4.11)

(ii) The residue from 4,5-dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole (1.292 g, 10mM) and p-nitrobenzenediazonium fluoroborate (4.738 g, 20 mM) consisted of two products. The products were boiled in chloroform in the presence of alumina for 30 minutes, to convert all the material into one compound. Chromatography

(10 x 3.5 cm, column I) with ether gave pale yellow eluates. Rechromatography (10 x 2 cm) with ether gave a trace of a yellow compound which was discarded. Ether:methanol (19:1) gave a slower-running yellow product.

Elution of column I with ether:methanol (19:1) afforded a further quantity of the slow-running yellow product. Crystallisation of this material from benzene gave 5, 6-dimethyl-3-p-nitrophenyl-6H-3aλ^4-thia-1, 2, 3, 4, 6-pentaazapentalene (67b) (825 mg, 30%) as yellow platelets, which sintered at 170°, decrepitated from 191°, then melted and decomposed from 206-212°.

Found: C 43.0; H 3.5; N 30.0

$C_{10}H_{10}N_6SO_2$ requires: C 43.2; H 3.6; N 30.2

Accurate mass determination: 278.0600

$C_{10}H_{10}N_6SO_2$ requires: 278.0586

^1H nmr: see Table 4

uv spectrum (methanol): λ_{max} (nm) 391 (logε 4.27), 276 (3.85), 219 (4.16), 207 (4.12)

(iii) The residue from 4, 5-dihydro-5-imino-4-methyl-3-methylthio-1, 2, 4-thiadiazole (1.613 g, 10 mM) with benzenediazonium fluoroborate (7.677 g, 40 mM) was chromatographed (20 x 2.7 cm). Benzene gave 6-methyl-5-methylthio-3-phenyl-6H-3aλ^4-thia-1, 2, 3-4, 6-pentaazapentalene (67c), (298 mg, 11.2%) as yellow rods from hexane, mp 126°, with decomposition.

Found: C 45.4; H 4.1; N 26.5

$C_{10}H_{11}N_5S_2$ requires: C 45.3; H 4.2; N 26.3

Accurate mass determination: 265.0446

$C_{10}H_{11}N_5S_2$ requires: 265.0456

^1H nmr: see Table 4

uv spectrum: λ_{max} (nm) 368sh (log ε 3.78), 326 (4.01), 269sh (3.75), 232pl (4.28), 208sh (4.13)

(iv) The residue from 4,5-dihydro-5-imino-4-methyl-3-methylthio-1,2,4-thiadiazole (1.613 g, 10 mM) with p-nitrobenzenediazonium fluoroborate (9.477 g, 40 mM) was chromatographed (20 x 3.5 cm). The rather insoluble material was put onto the column in a large volume of warm benzene. The column was eluted with cold benzene, then ether, which gave 6-methyl-5-methylthio-3-p-nitrophenyl-6H-3aλ^4-thia-1,2,3,4,6-pentaazapentalene (67d) (1.022 g, 51%) as yellow rods from benzene, mp 232-234° with decomposition, and sintering from 220°.

Found: C 38.7; H 3.1; N 27.5

$C_{10}H_{10}N_6S_2O_2$ requires: C 38.7; H 3.2; N 27.1

Accurate mass determination: 310.0298

$C_{10}H_{10}N_6S_2O_2$ requires: 310.0307

^1H nmr: see Table 4

uv spectrum (methanol, qualitative): λ_{max} (nm) 385, 340sh, 290, 238, 213, 206

b. Synthesis of 1,2,4-Trisubstituted-1H-3aλ^4-thia-1,3,4,6-tetraazapentalenes

(i) A solution of phosphoryl chloride (1.69 g, 1 ml, 11 mM) in dimethylformamide (10 ml) was stirred at room temperature for

10 minutes. 4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole (1.292 g, 10 mM) in dimethylformamide (25 ml) was added over a period of several minutes. The mixture was stirred for 30 minutes, when aqueous methylamine solution (100 ml) was added. After 10 minutes, the mixture was poured into water and extracted twice with methylene chloride. The extracts were washed with water (x 6) dried and evaporated to give a white solid. Chromatography (20 x 2 cm) with ether gave 1,2,4-trimethyl-1H-3aλ^4-thia-1,3,4,6-tetraazapentalene (71a) (392 mg, 23%) as white plates from cyclohexane, mp 128-132°.

Found: C 42.0; H 5.7; N 32.8

$C_6H_{10}N_4S$ requires: C 42.3; H 5.9; N 32.9

Accurate mass determination: 170.0616

$C_6H_{10}N_4S$ requires: 170.0626

^1H nmr: see Table 6

uv spectrum: λ_{max} (nm) 294 (logε 3.98), 208 (3.82)

(ii) A solution of phosphoryl chloride (1.69 g, 1 ml, 11 mM) in dimethylformamide (10 ml) was stirred at room temperature for 10 minutes, then added slowly to a solution of 5-amino-4-methyl-3-methylthio-4H-1,2,4-thiadiazolium iodide (2.982 g, 10 mM) and triethylamine (1.11 g, 1.53 ml, 11 mM) in dimethylformamide (40 ml). The mixture was stirred for 30 minutes, when aqueous methylamine solution (100 ml) was added. After 10 minutes, the mixture was poured into water, extracted with benzene

(2 x 500 ml), washed with water (x 6), dried and evaporated. The resulting pale brown oil was dissolved in benzene, boiled with active charcoal for a few minutes, filtered through a bed of "Hyflo Supercel" and the benzene evaporated off. The resulting colourless oil was triturated with petrol to give 1,4-dimethyl-2-methylthio-1H-3aλ^4-thia-1,3,4,6-tetraazapentalene (71b) (1.147 g, 56%) as white spars, mp 79-82.5°.

Found: C 35.8; H 5.0; N 27.4

$C_6H_{10}N_4S_2$ requires: C 35.6; H 5.0; N 27.7

Accurate mass determination: 202.0337

$C_6H_{10}N_4S_2$ requires: 202.0347

^1H nmr: see Table 6

uv spectrum: λ_{max} (nm) 297 (log ε 3.96), 223 (4.04), 208sh (3.92)

2. Synthesis of Oxa- and Selena-thiaazapentalenes

a. Preparation of 5-Acetamino-3-methyl-1,2,4-thiadiazole (73)

5-Amino-3-methyl-1,2,4-thiadiazole (5.758 g, 50 mM) was boiled with acetic anhydride (50 ml) for 30 minutes. The remaining acetic anhydride was evaporated off under reduced pressure, the last traces being removed by azeotropic distillation with toluene. The residual solid was recrystallised from benzene (3 crops) to give 5-acetamino-3-methyl-1,2,4-thiadiazole (73) (7.364 g, 94%) as white microprisms, mp 147-147.5°.

Found: C 38.0; H 4.3; N 27.0

$C_5H_7N_3SO$ requires: C 38.2; H 4.5; N 26.7

Accurate mass determination: 157.0307

$C_5H_7N_3SO$ requires: 157.0310

^1H nmr ($CDCl_3$): δ 2.24 (3H, COMe), 2.45 (3H, 3-Me), 3.35 (1H, br, NH)

b. Synthesis of 2,5,6-Trimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalene (75)

(i) Methylation of 5-Acetamino-3-methyl-1,2,4-thiadiazole

To a solution of 5-acetamino-3-methyl-1,2,4-thiadiazole (1.572 g, 10 mM) in dry benzene (80 ml) was added methyl fluorosulphonate (2.82 g, 1.62 ml, 20 mM). The mixture was refluxed for 30 minutes. On cooling, a glass formed. The solvent was decanted off, and the glass was dissolved in water, then treated with excess sodium carbonate solution. This aqueous solution was extracted with benzene (x 2), the extracts washed with water (x 3) dried and evaporated. The residue was purified by chromatography (silica, 20 x 2.7 cm). Ether gave a trace of an unidentified product, while ether:methanol (49:1, 500 ml) afforded 2,5,6-trimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalene (75) (602 mg, 35%) as white spars from benzene, mp 147.5-148.5°.

Found: C 42.1; H 5.3; N 24.7

$C_6H_9N_3OS$ requires: C 42.1; H 5.3; N 24.5

Accurate mass determination: 171.0473

$C_6H_9N_3OS$ requires: 171.0466

^{1}H nmr ($CDCl_3$): see Table 5

uv spectrum (methanol): λ_{max} (nm) 281 ($\log \varepsilon$ 4.04), 205 (3.84)

(ii) Acetylation of 4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole

4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole (1.292 g, 10 mM) was stirred for 30 minutes in acetic anhydride (25 ml). The mixture was extracted with benzene (x 2), washed with water (x 2) dried and evaporated. Crystallisation of the residue from benzene gave 2,5,6-trimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalene (75) (800 mg, 47%) as white spars, mp 147-148°, mixed mp 147.5-148.5°. Mass spectrum, ^{1}H nmr spectrum identical to previous sample.

c. Preparation of 5-Formamino-3-methyl-1,2,4-thiadiazole (77)

To a solution of 5-amino-3-methyl-1,2,4-thiadiazole (2.303 g, 20 mM) in xylene (100 ml) was added formic acid (2.30 g, 1.9 ml, 50 mM). The mixture was refluxed for 24 hours, when the solvent was removed under reduced pressure. The residual white solid consisted of a mixture of unreacted starting material and the desired product, in the approximate ratio of 1:7. Two successive crystallisations of this material from ethanol, with charcoal screening gave 5-formamino-3-methyl-1,2,4-thiadiazole (77), (1.494 g, 52%) as white microprisms, mp 189° (sublimes).

Found: C 33.3; H 3.3; N 29.3

$C_4H_5N_3OS$ requires: C 33.6; H 3.5; N 29.3

Accurate mass determination: 143.0145

$C_4H_5N_3OS$ requires: 143.0153

^1H nmr (DMSO-D_6): δ 2.46 (3H, 3-Me), 8.74 (1H, CHO), 12.85 (1H, br, NH)

d. Synthesis and Attempted Synthesis of 5,6-Disubstituted-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalenes

(i) Methylation of 5-Formamino-3-methyl-1,2,4-thiadiazole

5-Formamino-3-methyl-1,2,4-thiadiazole (1.432 g, 10 mM) was ground up and suspended in dry chloroform (200 ml). To this was added methyl fluorosulphonate (2.82 g, 1.62 ml, 20 mM), and the mixture was stirred for 18 hours, during which time a tarry oil formed around the sides of the flask. The chloroform was decanted off, and treated with ether, to precipitate any salt which had dissolved in the chloroform. None was obtained. The oil in the flask was dissolved in water, and excess sodium carbonate added. The resulting solution was extracted into methylene chloride (2 x 250 ml), washed with water (x 3) and dried. The colourless product was purified by chromatography (20 x 2 cm). Elution with ether:methanol (49:1) afforded 5,6-dimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalene (79a) (290 mg, 18.5%) as white prisms from cyclohexane, mp 101-101.5°.

Found: C 38.1; H 4.4; N 26.4

$C_5H_7N_3SO$ requires: C 38.2; H 4.5; N 26.7

Accurate mass determination: 157.0302

$C_5H_7N_3SO$ requires: 157.0310

^1H nmr: see Table 5

uv spectrum: λ_{max} (nm) 284 (log ε 3.99), 235 (3.09), 206 (3.85)

(ii) Attempted Formylation of the Vilsmeier Salts (70)

A solution of phosphoryl chloride (1.69 g, 1 ml, 11 mM) in dimethylformamide (10 ml) was stirred at room temperature for 10 minutes. 4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole (1.292 g, 10 mM) in dimethylformamide (25 ml) was added slowly. The mixture was stirred for 30 minutes, when 2M sodium hydroxide solution (100 ml) was added. After 10 minutes the mixture was poured into water and extracted with methylene chloride (x 2). The extracts were washed with water (x 6), dried and evaporated. No useful material was obtained.

A solution of phosphoryl chloride (1.69 g, 1 ml, 11 mM) in dimethylformamide (10 ml) was stirred at room temperature for 10 minutes, then added slowly to a solution of 5-amino-4-methyl-3-methylthio-4H-1,2,4-thiadiazolium iodide (2.982 g, 10 mM) and methylamine (1.11 g, 1.55ml, 11 mM), in dimethylformamide (40ml). The mixture was stirred for 30 minutes, and 2M sodium hydroxide solution (100 ml) was added. After 10 minutes the mixture was poured into water, extracted with benzene (x 2), washed with water (x 6), dried and evaporated. A pale brown oil was obtained. This was identified as 4,5-dihydro-5-imino-4-methyl-3-methylthio-1,2,4-thiadiazole (66b) (810 mg, 50%), identical to a sample previously prepared (mass spectrum, ^{1}H nmr spectrum).

(iii) Formylation of 4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole

4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole (1.292 g, 10 mM) was stirred in formic acid (50 ml) for 30 minutes. The formic acid was distilled off under reduced pressure, the last traces being removed by azeotropic distillation with toluene. The product, 5,6-dimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalene (79a) (884 mg, 56%) crystallised as white prisms from cyclohexane, mp 101-101.5°, mixed mp 101-101.5°. The mass spectrum and ^{1}H nmr spectrum were identical to those of the sample prepared in (i) above.

(iv) Hydrolysis of 1,4-Dimethyl-2-methylthio-1H-3aλ^4-thia-1,3,4,6-tetraazapentalene

1,4-Dimethyl-2-methylthio-1H-3aλ^4-thia-1,3,4,6-tetraazapentalene (2.031 g, 10 mM) was dissolved in benzene and chromatographed (silica, 40 x 2.7 cm). The column was eluted with benzene (500 ml) followed by 100 ml portions of benzene:ether (9:1, 4:1, 1:1), which were discarded. Ether afforded 6-methyl-5-methylthio-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalene (79b) (660 mg, 35%) as white prisms from cyclohexane, mp 134-136°.

Found: C 31.6; H 3.7; N 22.2

$C_5H_7N_3OS_2$ requires: C 31.7; H 3.7; N 22.2

Accurate mass determination: 189.0025

$C_5H_7N_3OS_2$ requires: 189.0030

^{1}H nmr: see Table 5

uv spectrum: λ_{max} (nm) 290 (log ε 3.91), 224. (4.09), 202 (3.69)

e. Attempted Synthesis of 5,6-Dimethyl-6H-3aλ^4-thia-3-selena-1,4,6-triazapentalene

A solution of phosphoryl chloride (1.69 g, 1 ml, 11 mM) in dimethylformamide (10 ml) was stirred at room temperature for 10 minutes. 4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole (1.292 g, 10 mM) in dimethylformamide (25 ml) was slowly added. The mixture was stirred for 30 minutes, when sodium hydrogen selenide solution ($\equiv$ 60 mM NaSeH) was added. Red selenium was immediately deposited. After 10 minutes the mixture was poured into water, extracted twice with benzene, and the extracts washed with water (x 6), dried and evaporated. The yellow residue was chromatographed (10 x 2.7 cm). Benzene brought forth pale yellow eluates which were discarded, followed by darker yellow eluates which afforded dimethylselenoformamide (83), as a yellow oil, bp 80°C at reduced pressure (cf. lit.[172] 79° at 0.4 mm).

^{1}H nmr ($CDCl_3$): 3.30 (3H, N-Me), 3.35 (3H, N-Me), 10.61 (1H, CHSe),

Mass spectrum: M^+ at 139

3. Synthesis of Dithiaazapentalenes

a. Synthesis of 5,6-Disubstituted-6H-3,3aλ^4-dithia-1,4,6-triaza-pentalenes

(i) Thioformylation of the Vilsmeier Salts (70)

A solution of phosphoryl chloride (1.69 g, 1 ml, 11 mM) in dimethylformamide (10 ml) was stirred at room temperature for 10 minutes. 4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole

(1.292 g, 10 mM) in dimethylformamide was slowly added. The mixture was stirred for 30 minutes, when sodium hydrogen sulphide solution (4M, 100 ml) was added. After 10 minutes the mixture was poured into water, extracted with benzene (x 2), washed with water (x 6) dried and evaporated. Chromatography (20 x 2.7 cm) of the residue with benzene gave 5,6-dimethyl-6H-3,3aλ^4-dithia-1,4,6-triazapentalene (84a) (612 mg, 35%) as yellow needles from cyclohexane, mp 145.5-147°.

Found: C 34.5; H 4.0; N 24.2; S 37.0

$C_5H_7N_3S_2$ requires: C 34.7; H 4.1; N 24.2; S 37.0

Accurate mass determination: 173.0077

$C_5H_7N_3S_2$ requires: 173.0081

^1H nmr: see Table 7

uv spectrum: λ_{max} (nm) 349 (log ε 4.05), 224 (4.15)

A solution of phosphoryl chloride (1.69 g, 1 ml, 11 mM) in dimethylformamide (10 ml) was stirred at room temperature for 10 minutes, then added slowly to a solution of 5-amino-4-methyl-3-methylthio-4H-1,2,4-thiadiazolium iodide (2.982 g, 10 mM) and triethylamine (1.11 g, 1.53 ml, 11 mM) in dimethylformamide (40 ml). The mixture was stirred for 30 minutes, when sodium hydrogen sulphide solution (4M, 100 ml) was added. After 10 minutes the mixture was poured into water, extracted with benzene (x 2), washed with water (x 6) dried and evaporated. Chromatography (20 x 2.7 cm) of the residue with benzene gave 6-methyl-5-methylthio-6H-3,3aλ^4-dithia-1,4,6-triazapentalene (84b) (1.188 g, 58%) as

yellow needles from cyclohexane, mp 94-95°

Found: C 29.6; H 3.6; N 20.3

$C_5H_7N_3S_3$ requires: C 29.3; H 3.4; N 20.5

Accurate mass determination: 204.9791

$C_5H_7N_3S_3$ requires: 204.9802

^1H nmr: see Table 7

uv spectrum: λ_{max} (nm) 353 (log ε 4.02), 277 (3.31), 231 (4.34), 217sh (4.25)

(ii) Thionation of 5,6-Dimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triaza-pentalene

To a solution of 5,6-dimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalene (314 mg, 2 mM) in pyridine (20 ml) was added phosphorus pentasulphide (444 mg, 2 mM). The mixture was refluxed for 30 minutes, allowed to cool and the product was poured into water, extracted with benzene (x 2), washed with water (x 3) dried and evaporated. The residue was purified by chromatography (20 x 2.0 cm). Elution with benzene afforded 5,6-dimethyl-6H-3,3aλ^4-dithia-1,4,6-triazapentalene (84a) (195 mg, 56%) as yellow needles from cyclohexane, mp 145.5-147°, mixed mp 145.5-146.5°, mass spectrum and ^1H nmr spectrum identical to that of the previously prepared sample.

b. Synthesis of 2,5,6-Trisubstituted-6H-3,3aλ^4-dithia-1,4,6-triaza-pentalenes

(i) Thionation of 2,5,6-Trimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triaza-pentalene

2,5,6-Trimethyl-6H-3-oxa-3aλ^4-thia-1,4,6-triazapentalene

(342 mg, 2 mM) was dissolved in toluene (20 ml) and phosphorus pentasulphide (444 mg, 2mM) added. The mixture was refluxed for 30 minutes, allowed to cool, then poured into water, extracted with benzene (x 2), washed with water (x 3) dried and evaporated. The residue was purified by chromatography (30 x 2.0 cm). Benzene gave a pale yellow product, probably sulphur, which was discarded. Benzene:ether (9:1) afforded 2,5,6-trimethyl-6H-3,3aλ^4-dithia-1,4,6-triazapentalene (86) (148 mg, 40%) as yellow spars from cyclohexane, mp 184-185°.

Found: C 38.6; H 4.6; N 22.6

$C_6H_9N_3S_2$ requires: C 38.5; H 4.8; N 22.4

Accurate mass determination: 187.0232

$C_6H_9N_3S_2$ requires: 187.0238

^1H nmr: see Table 7

uv spectrum: λ_{max} (nm) 345 (log ε 3.87), 280 (3.28), 267sh (3.15), 222 (4.14)

(ii) The Reaction of Carbon Disulphide with the Salts (65)

General Method:-

Triethylamine (4.05 g, 5.57 ml, 40 mM) and carbon disulphide (1.53 g, 1.20 ml, 20 mM) were added to a solution of the 1,2,4-thiadiazolium iodide (10 mM) in acetonitrile (100 ml). The mixture was stirred at room temperature for 10 minutes, then methyl iodide (5.67 g, 2.50 ml, 40 mM) was added and the solution stirred for a further 10 minutes. During this time it decolourised from red to pale yellow. The mixture was poured into water, extracted with benzene (x 2), washed with water (x 3) dried and

evaporated. The residue was purified by chromatography (30 x 2.7 cm). Elution with petrol gave a small quantity of a pale yellow impurity, which was discarded. Benzene gave the desired product.

5-Amino-3,4-dimethyl-4H-1,2,4-thiadiazolium iodide (2.571 g, 10 mM) gave 5,6-dimethyl-2-methylthio-6H-3,3aλ^4-dithia-1,4,6-triazapentalene (88a) (706 mg, 32%) as pale yellow spars from cyclohexane, mp 152.5-153.5°.

Found: C 32.7; H 4.1; N 19.2

$C_6H_9N_3S_3$ requires: C 32.9; H 4.1; N 19.2

Accurate mass determination: 218.9942

$C_6H_9N_3S_3$ requires: 218.9958

^{1}H nmr: see Table 7

uv spectrum: λ_{max} (nm) 338 (logε 4.23), 315 (4.09), 224 (4.27)

5-Amino-4-methyl-3-methylthio-4H-1,2,4-thiadiazolium iodide (2.892 g, 10 mM) gave 6-methyl-2,5-dimethylthio-6H-3,3aλ^4-dithia-1,4,6-triazapentalene (88b) (475 mg, 18%) as pale yellow spars from cyclohexane, mp 142-143°.

Found: C 28.9; H 3.8; N 16.5

$C_6H_9N_3S_4$ requires: C 28.7; H 3.6; N 16.7

Accurate mass determination: 250.9670

$C_6H_9N_3S_4$ requires: 250.9679

^{1}H nmr: see Table 7

uv spectrum: λ_{max} (nm) 343 (logε 4.23), 319 (4.05), 252sh (3.86), 228 (4.45)

4. Attempted Synthesis of 5,6-Dimethyl-6H-3,3aλ^4-dithia-1,2,4,6-tetraazapentalene

a. Preparation of 5,6-Dimethyl-6H-3-oxa-3aλ^4-thia-1,2,4,6-tetraazapentalene (89)

The following modification of Goerdeler's method[107] was used:-

5-Amino-3,4-dimethyl-4H-1,2,4-thiadiazolium iodide (2.571 g, 10 mM) was dissolved in $^N/_2$ hydrochloric acid (50 ml), the mixture cooled to 0°, and sodium nitrite (1.381 g, 20 mM) added. The iodine which was liberated was filtered off under suction, and washed with a small quantity of $^N/_2$ hydrochloric acid. Sodium nitrite (690 mg, 10 mM) was added to the filtrates, which were then left to stand for 2 hours. The product which had precipitated out was filtered off, dried and recrystallised from benzene. The mother liquors were combined with the aqueous filtrates, and extracted with benzene (x 2). The extracts were washed with water, sodium bicarbonate solution, then with more water, dried and evaporated. Chromatography (20 x 2 cm) with ether gave yellow eluates which afforded 5,6-dimethyl-6H-3-oxa-3aλ^4-thia-1,2,4,6-tetraazapentalene (89) (total yield 921 mg, 58%) as yellow plates from benzene, mp 156-158°.

Found: C 30.5; H 3.9; N 35.6

$C_4H_6N_4OS$ requires: C 30.4; H 3.8; N 35.4

Accurate mass determination: 158.0255

$C_4H_6N_4OS$ requires: 158.0262

^{1}H nmr ($CDCl_3$): δ 2.67 (3H, 5-Me), 4.04 (3H, 4-Me)

uv spectrum (methanol); λ_{max} (nm) 314 (log ε 3.80), 247 (3.34), 211 (3.73)

b. Attempted Thionation of 5,6-Dimethyl-6H-3-oxa-3aλ^4-thia-1,2,4,6-tetraazapentalene (89)

To a solution of 5,6-dimethyl-6H-3-oxa-3aλ^4-thia-1,2,4,6-tetraazapentalene (791 mg, 5 mM) in pyridine (50 ml) was added phosphorus pentasulphide (1.110 g, 5 mM). The mixture was refluxed for 10 minutes, and became colourless. It was poured into water, and extracted with benzene (x 2). The extracts were washed with water (x 3), dried and evaporated. Chromatography (30 x 2 cm) of the residue with petrol removed traces of sulphur which were present. Benzene afforded 3,4-dimethyl-4H-1,2,4-thiadiazole-5-thione (91) (318 mg, 43%) as white prisms from hexane, mp 100-100.5°.

Found: C 32.8; H 4.0; N 19.2; S 44.1

$C_4H_6N_2S_2$ requires: C 32.8; H 4.1; N 19.2; S 43.9

Accurate mass determination: 145.9963

$C_4H_6N_2S_2$ requires: 145.9972

^{1}H nmr ($CDCl_3$): δ 2.51 (3H, 3-Me), 3.63 (3H, 4-Me)

5. The Reaction of 4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole with Iso(thio)cyanate

General Method:-

4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole (1.292 g, 10 mM) was dissolved in benzene (100 ml) and the iso(thio)-cyanate (12 mM) was added. The solution was left standing for 30 minutes, during which time the product began to crystallise out. The product was filtered off, and the mother liquors were evaporated to give a further quantity of the product.

Phenyl isothiocyanate (1.62 g, 1.43 ml, 12 mM) gave

2-aminophenyl-5, 6-dimethyl-6H-3, 3aλ^4-dithia-1, 4, 6-triaza-pentalene (94) (2.517g, 95%) as white microneedles from ethanol, mp 161.5-163°.

Found: C 49.6: H 4.5; N 21.5

$C_{11}H_{12}N_4S_2$ requires: C 50.0; H 4.6; N 21.2

Accurate mass determination: 264.0491

$C_{11}H_{12}N_4S_2$ requires: 264.0503

^1H nmr ($CDCl_3$): δ 2.49 (3H, 5-Me), 3.68 (3H, 6-Me), 7.11-7.68 (5H, m, Ph), 8.46 (1H, br, NH)

uv spectrum (methanol): λ_{max} (nm) 320 (log ε 4.36), 226 (4.40), 215sh (4.39)

Phenyl isocyanate (1.43 g, 1.30 ml, 12 mM) gave 2-amino-phenyl-5, 6-dimethyl-6H-3-oxa-3aλ^4-thia-1, 4, 6-triazapentalene (98) (1.841 g, 74%) as white microplates from benzene, mp 204-205°, with sintering from 170°.

Found: C 53.1; H 4.7; N 23.0

$C_{11}H_{12}N_4OS$ requires: C 53.2; H 4.9; N 22.6

Accurate mass determination: 248.0739

$C_{11}H_{12}N_4OS$ requires: 248.0732

^1H nmr ($CDCl_3$): δ 2.44 (3H, 5-Me), 3.60 (3H, 6-Me), 7.02-7.60 (6H, m, Ph and NH)

uv spectrum (methanol): λ_{max} (nm) 291 (log ε 4.46), 238 (3.88), 205 (4.27)

6. The Reaction of Thiophosgene with 4,5-Dihydro-5-imino-1,2,4-thiadiazoles

Triethylamine (1.012 g, 1.39 ml, 10 mM) and thiophosgene (230 mg, 0.15 ml, 2 mM) were added to a solution of the imine (5 mM) in sodium-dry benzene (200 ml). The mixture was stirred at room temperature for one hour, and turned yellow. The mixture was poured into water, extracted with benzene (x 2), washed with water (x 3) dried and evaporated. The residue was purified by chromatography (30 x 2 cm). Elution with ether:methanol (19:1) gave pale yellow eluates containing the product.

(i) 4,5-Dihydro-5-imino-3,4-dimethyl-1,2,4-thiadiazole (646 mg, 5 mM) gave 1,3-bis-(3,4-dimethyl-1,2,4-thiadiazol-5-ylidene)acetone (102a) (57 mg, 10%) as pale yellow prisms from benzene, mp 276-278.5°.

Accurate mass determination: 284.0501

$C_9H_{12}N_6OS_2$ requires: 284.0514

^1H nmr ($CDCl_3$, saturated solution): δ 2.53 (6H, br, 2 x C-Me), 3.85 (6H, br, 2 x N-Me)

A satisfactory analysis was not obtained for this compound.

(ii) 4,5-Dihydro-5-imino-4-methyl-3-methylthio-1,2,4-thiadiazole (807 mg, 5 mM) gave 1,3-bis-(4-methyl-3-methylthio-1,2,4-thiadiazol--5-ylidene)acetone (102b) (504 mg, 72%) as pale yellow needles from acetonitrile, mp 267-268°.

Found: C 31.5; H 4.0; N 23.8

$C_9H_{12}N_6OS_4$ requires: C 31.0; H 3.5; N 24.1

Accurate mass determination: 347.9945

$C_9H_{12}N_6OS_4$ requires: 347.9955

^1H nmr ($CDCl_3$, saturated solution): δ 2.68 (6H, br, 2 x C-Me),

3.78 (6H, br, 2 x N-Me)

REFERENCES

1. N. Lozac'h, Adv. Het. Chem., 1971, 13, 161
2. E. Klingsberg, Q. Rev., 1969, 23, 537
3. D.H. Reid, "Organic Compounds of Sulphur, Selenium and Tellurium", The Chemical Society, London, 1970, 1, 321
4. R.J.S. Beer, "Organic Compounds of Sulphur, Selenium and Tellurium", The Chemical Society, London, 1972, 2, 497
5. R.J.S. Beer, "Organic Compounds of Sulphur, Selenium and Tellurium", The Chemical Society, London, 1975, 3, 494
6. R.J.S. Beer, "Organic Compounds of Sulphur, Selenium and Tellurium", The Chemical Society, London, 1977, 4, 300
7. L.K. Hansen and A. Hordvik, Acta Chem. Scand., 1973, 27, 411
8. A. Hordvik, Acta Chem. Scand., 1966, 20, 1885
9. L. Pauling, "The Nature of the Chemical Bond", 3rd Edn., Cornell University Press, Ithaca, New York, 1960
10. D.W.J. Cruickshank, Acta Cryst., 1970, B26, 1260
11. S. Bezzi, C. Garbuglio and M. Mammi, Nature, 1958, 182, 247
12. S. Bezzi, C. Garbuglio, M. Mammi, and R. Bardi, Acta Cryst., 1960, 13, 1048
13. F. Leung and S. Nyburg, Chem. Comm., 1969, 137
14. A. Hordvik, O. Sjolset and L.J. Saethre, Acta Chem. Scand., 1973, 27, 379
15. B. Birkness, A. Hordvik and L.J. Saethre, Acta Chem. Scand., 1973, 27, 382
16. O. Hjellum and A. Hordvik, Acta Chem. Scand., 1973, 27, 2666
17. A. Hordvik, Acta Chem. Scand., 1971, 25, 1583

18. P.L. Johnston, E.C. Llaguno and I.C. Paul, J.C.S. Perkin II, 1976, 234

19. B. Birkness, A. Hordvik and L.J. Saethre, Acta Chem. Scand., 1975, 29A, 195

20. A. Hordvik and L.J. Saethre, Acta Chem. Scand., 1975, 29A, 136

21. A. Hordvik and L.J. Saethre, Israeli J. Chem., 1972, 10, 239

22. G. Traverso, Chem. Ber., 1958, 91, 1224

23. A. Hordvik, E. Sletten and J. Sletten, Acta Chem. Scand., 1969, 23, 1852

24. A. Hordvik and K. Julshamn, Acta Chem. Scand., 1971, 25, 1835

25. A. Hordvik, O. Sjolset and L.J. Saethre, Acta Chem. Scand., 1976, 26, 1297

26. E.C. Llaguno and I.C. Paul, J.C.S. Perkin II, 1976, 228

27. E.C. Llaguno, C.T. Mabuni and I.C. Paul, J.C.S. Perkin II, 1976, 239

28. N. Nummi, R. Bardi, G. Traverso and S. Bezzi, Nature, 1961, 192, 1282

29. A. Hordvik, E. Sletten and J. Sletten, Acta Chem. Scand., 1969, 23, 1377

30. P.L. Johnstone, K.I.G. Reid and I.C. Paul, J. Chem. Soc. (B), 1971, 946

31. A. Hordvik and L. Milje, Acta Chem. Scand., 1973, 27, 511

32. F.C. Leung and S.C. Nyburg, Can. J. Chem., 1972, 50, 324

33. A. Hordvik and K. Julsham, Acta Chem. Scand., 1972, 26, 343

34. L.K. Hansen and K. Tomren, Acta Chem. Scand., 1977, 31A, 292

36. L.K. Hansen and L.P. Darmo, Acta Chem. Scand., 1977, 31A, 412

36. G. Pfister-Guillouzo and N. Lozac'h, Bull. Soc. Chim. Fr., 1964, 3254

37. J.G. Dingwall, S. McKenzie and D.H. Reid, J. Chem. Soc. (C), 1968, 2543

38. J.G. Dingwall, PhD Thesis, University of St. Andrews, 1968

39. A.S. Ingram, D.H. Reid and J.D. Symon, J.C.S. Perkin I, 1974, 242

40. D.H. Reid, J. Chem. Soc. (C), 1971, 3187

41. R.M. Christie, D.H. Reid and R. Walker, J.C.S. Perkin I, 1978, 195

42. R.J.S. Beer and I. Hart, J.C.S. Chem. Comm., 1977, 143

43. H.G. Hertz, G. Traverso and W. Waltern, Annalen, 1959, 625, 43

44. H. Behringer and J. Falkenberg, Chem.Ber., 1969, 102, 1580

45. D. Paquer, M. Perrier and J. Vialle, Bull.Soc.Chim.Fr.,1970, 4517

46. S. McKenzie and D.H. Reid, J. Chem. Soc. (C), 1970, 145

47. R.K. Mackie, S. McKenzie, D.H. Reid and R.G. Webster, J.C.S. Perkin I, 1973, 657

48. D.H. Reid and R.G. Webster,J.C.S. Perkin I, 1972, 1447

49. J.G. Dingwall, A.S. Ingram, D.H. Reid and J.D. Symon, ibid., 1973, 2351

50. R. Pinel, Y. Mollier and N. Lozac'h, Bull.Soc. Chim. Fr., 1966, 3187

51. R.D. Lapper and A.J. Poole, Tet. Lett., 1974, 2783

52. C. Pedersen and K. Schaumburg, Org. Mag. Res., 1974, 6, 586

53. D.T. Clark, D. Kilcast and D.H. Reid, Chem. Comm., 1971, 638

54. D.T. Clark, Int. J. Sulphur Chem., 1972, C, 7, 11

55. B.J. Lindberg, Int. J. Sulphur Chem., 1972, C, 7, 35

56. T. Pedersen, S. Skaarup and C. Pedersen, Acta Chem. Scand., 1977, 31B, 711

57. S. Bezzi, G. Garbuglio, M. Mammi and G. Traverso, Gazz. Chem. Ital., 1958, 88, 1226

58. G. Giacometti and G. Rigatti, J. Chem. Phys., 1959, 30, 1633

59. E.M. Shustorovich, J. Gen. Chem. USSR, 1959, 29, 2424; Chem. Abs., 1960, 54, 8269

60. G. Pfister-Guillouzo and N. Lozac'h, Bull. Soc. Chim. Fr., 1963, 153

61. K. Maeda, Bull. Chem. Soc. Japan, 1960, 33, 1466

62. K. Maeda, Bull. Chem. Soc. Japan, 1961, 34, 785

63. K. Maeda, Bull. Chem. Soc. Japan, 1961, 34, 1116

64. R.A.W. Johnstone and S.D. Ward, Theor. Chim. Acta, 1969, 14, 420

65. R. Gleiter and R. Hoffmann, Tet., 1968, 24, 5899

66. L.K. Hansen, A. Hordvik and L.J. Saethre, J.C.S. Chem. Comm., 1972, 222

67. M.H. Palmer and R.H. Findlay, Tet. Lett., 1972, 4165

68. M.H. Palmer and R.H. Findlay, J.C.S. Perkin II, 1974, 1885

69. M.H. Palmer and R.H. Findlay, J. Mol. Struct., 1977, 37, 229-236

70. C.A. Coulson, Nature, 1969, 221, 1106

71. R.J. Hach and R.E. Randle, J. Am. Chem. Soc., 1951, 73, 4321

72. J.I. Musher, Angew. Chem. Internat. Edn., 1969, 8, 54

73. O. Andresen and C. Römming, Acta Chem. Scand., 1962, 16, 1882

74. S.L. Lawton and R.A. Jacobsen, Inorg. Chem., 1968, 7, 2124

75. T. Migchelsen and A. Vos, Acta Cryst., 1967, 23, 796

76. T. Bernstein and F.H. Herbestein, Acta Cryst., 1958, B24, 1640

77. O. Foss and S. Hauge, Acta Chem. Scand, 1963, 17, 1807

78. S. Hauge, Acta Chem. Scand., 1971, 25, 1134

79. F. Arndt, P. Nachtwey and J. Pusch, Chem. Ber., 1925, 58, 1633

80. M. Stavaux and N. Lozac'h, Bull. Soc. Chim. Fr., 1967, 2082

81. G. Traverso, Ann. Chim. (Rome), 1954, 44, 1018

82. G. Traverso, Ann. Chim. (Rome), 1955, 45, 687

83. H. Behringer, M. Ruff and R. Weidenmann, Chem. Ber., 1964, 97, 1732

84. D. Leaver, W.A.H. Robertson and D.M. McKinnon, J. Chem. Soc., 1962, 5104

85. J.G. Dingwall, D.H. Reid and J.D. Symon, J. Chem. Soc. (C), 1970, 2412

86. C. Metayer, G. Duguay and H. Quinious, Bull. Soc. Chim. Fr., 1974, 163

87. E. Klingsberg, J. Org. Chem., 1968, 33, 2915

88. A. Grandin and J. Vialle, Bull. Soc. Chim. Fr., 1967, 1851

89. G. Lang and J. Vialle, Bull. Soc. Chim. Fr., 1967, 2865

90. A.G. Briggs, J. Czyzewski and D.H. Reid , J.C.S. Perkin I, 1979, 2340

91. R.M. Christie and D.H. Reid, J.C.S. Perkin I, 1976, 228

92. J.L. Derocque and J. Vialle, Bull. Soc. Chim. Fr., 1967, 3079

93. J.L. Derocque, M. Perrier and J. Vialle, Bull. Soc. Chim. Fr., 1968, 2062

94. H. Behringer and D. Weber, Chem. Ber., 1964, 97, 2567

95. J.E. Oliver and R.T. Brown, J. Org. Chem., 1974, 39, 2228

96. R.M. Christie, D.H. Reid and R. Wolfe-Murray, J.C.S. Perkin I, 1979, 926

97. M. Perrier and J. Vialle, Bull. Soc. Chim. Fr., 1979, II, 205

98. K-T. Wei, I.C. Paul, R.J.S. Beer and A. Naylor, J.C.S. Chem. Comm., 1975, 264

99. R.J.S. Beer and A. Naylor, Tet. Lett., 1973, 2989

100. K.T. Potts and R. Armbruster, J. Org. Chem., 1970, 35, 1965

101. K.T Potts and R. Armbruster, J. Org. Chem., 1970, 36, 1846

102. J. Goerdeler and E.R. Erbach, Chem. Ber., 1962, 95, 1637

103. K.T. Potts and J. Kane, J. Org. Chem., 1973, 38, 3087

104. K.T. Potts and J. Kane, J. Org. Chem., 1975, 40, 2600

105. K. T. Potts and J. Kane, J. Org. Chem., 1974, 39, 3783

106. R.L.N. Harris, Aust. J. Chem., 1972, 25, 993

107. J. Goerdeler, A. Huppertz and K. Wember, Chem. Ber., 1954 1955, 87, 68

108. J. Goerdeler and K. Deselaers, Chem. Ber., 1958, 91, 1025

109. J. Goerdeler, K. Deselaers and A. Ginsberg. Chem. Ber., 1960, 93, 963

110. L.K. Hansen, Acta Chem. Scand., 1977, 31A, 855

111. J. Goerdeler and J. Ulmen, Chem. Ber., 1972, 105, 1568

112. K. Akiba et al, Angew. Chem. Internat. Edn., 1979, 18, 166

113. J. Goerdeler and W. Roth, Chem. Ber., 1963, 96, 534

114. O. Glemser et al, Z. Anorg. Chem., 357, 184

115. K. Akiba and S. Arai, Tet. Lett., 1978, 4117

116. K. Akiba, T. Tsuchiya and N. Inamoto, Tet. Lett., 1976, 1877

117. J.D. Symon, PhD Thesis, University of St.Andrews, 1970

118. K. Akiba, T. Tsuchiya and M. Ochiumi, Tet. Lett., 1975, 455

119. K. Akiba, T. Tsuchiya and M. Ochiumi, Tet. Lett., 1975, 459

120. K. Akiba, T. Tsuchiya and M. Ochiumi, Chem. Lett., 1976, 723-6

121. A.R. Butler, C. Glidewell and D.C. Liles, J.C.S. Chem. Comm., 1978, 652

122. C. Glidewell, personal communication

123. E. Fromm and R. Heyder, Chem. Ber., 1909, 42, 3804

124. A.R. Butler, J. Chem. Res. (S), 1978, 50; (M), 1978, 0855

125. C. Glidewell, A.R. Butler and D.C. Liles, Acta Cryst., 1978, B34, 2570

126. J.E. Oliver and A.B. De Milo, J. Org. Chem., 1974, 39, 2225

127. G.B. Carpenter, J. Chem. Ed., 1973, 40, 385

128. H.Z. Müller, Z. Chem., 1957, 7, 81

129. E. Klingsberg, Chem. Ind. (London), 1968, 1813

130. M. Stavaux and N. Lozac'h, Bull. Soc. Chim. Fr., 1968, 4273

131. M. Stavaux and N. Lozac'h, Bull. Soc. Chim. Fr., 1969, 4184

132. R. Kristensen and J. Sletten, Acta Chem. Scand., 1971, 25, 2366

133. R. Kristensen and J. Sletten, Acta Chem. Scand., 1973, 27, 2517

134. J. Sletten, Acta Chem. Scand., 1976, 30A, 661

135. J. Sletten, Acta Chem. Scand., 1975, 29A, 436

136. J. Sletten, Acta Chem. Scand., 1976, 30A, 397

137. G. Calaferri and R. Gleiter, J.C.S. Perkin II, 1975, 559

138. J. Sletten and M. Velsvik, Acta Chem. Scand., 1973, 27, 3881

139. J.J. O'Connor (ed) "Standard Handbook of Lubrication Engineering", McGraw-Hill Book Co., New York, 1968

140. J.L. Bolland, Q. Rev., 1949, 3, 1

141. G.A. Russell, J. Chem. Ed., 1959, 36, 111

142. K.U. Ingold, J. Inst. Pet., 1961, 47, 375

143. US Patent 2 816 116 Chem. Abs., 1959, 52, 7581

144. US Patent 2 653 910 Chem. Abs., 1957, 48, 10333

145. US Patent 2 995 569 Chem. Abs., 1961, 56, 5971

146. US Patent 2 763 908 Not listed in Chem. Abs.

147. US Patent 2 971 909 Chem. Abs., 1961, 55, 11832

148. US Patent 3 621 030 Chem. Abs., 1971, 76, 34257

149. US Patent 3 821 236 Chem. Abs., 1974, 81, 102634

150. US Patent 3 816 312 Chem. Abs., 1973, 79, 33408

151. Belgian Patent 823 391 Chem. Abs., 1975, 83, 150214

152. British Patent Application No. 52636/75, December 23rd, 1975

153. D.D. Perrin (ed) "Dissociation Constants of Organic Bases in Solution", Butterworths, London, 1965

154. Y. Mollier and N. Lozac'h, Bull. Soc. Chim. Fr., 1961 (614)

155. C. Paulmier, Y. Mollier and N. Lozac'h, Bull. Soc. Chim. Fr., 1965 (2463)

156. A.G. Briggs, MSc Thesis, University of St. Andrews, 1978

157. C. Pederson and C. Lohse, J.C.S. Perkin I, 1977, 994

158. C. Pederson and C. Lohse, J.C.S. Chem. Comm., 1973, 123

159. C. Pederson and C. Lohse, J. C.S. Perkin I, 1973, 2837

160. G. Calaferri et al, Helv. Chim. Acta, 1973, 56, 597

161. R. Gleiter et al, Tet. Lett., 1973, 1257

162. G. Calaferri et al, Helv. Chim. Acta, 1973, 56, 2584

163. J. Czyzewski, PhD Thesis, University of St. Andrews, 1977

164. D.L. Klayman and S.T. Griffin, J.Am.Chem.Soc., 1973, 95, 197

165. E. Klingsberg, J. Am. Chem. Soc., 1961, 83, 2934

166. J. Faust and R. Mayer, Annalen, 1965, 688, 150

167. N.J. Leonard (ed), Organic Synthesis, Chapman and Hall, London, 1956, 36, 64

168. L. Weintraub, S.R. Oles and N. Kalish, J. Org. Chem., 1968, 33, 1679

169. R. Levine and C.R. Hauser, J. Am. Chem. Soc., 1944, 66, 1768

170. J. Goerdeler, Chem. Ber., 1954, 87, 57

171. J. Goerdeler and P. Linden, Chem. Ber., 1956, 89, 2742

172. L. Brandsma, Bull. Chim. Soc. Belge., 1963, 72, 304